

**FUEL SPECIFICATIONS AND FUEL PROPERTY ISSUES
AND THEIR POTENTIAL IMPACT ON THE USE
OF ETHANOL AS A TRANSPORTATION FUEL**

Downstream Alternatives Inc.

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CONTENTS PAGE

Section 1	Background, Introduction, & Summary of Recommendations	1-1
	1.0 Background, Introduction, & Summary of Recommendations	1-2
Section 2	Ethanol Quality Issues	2-1
	2.0 Ethanol Quality Issues	2-2
	2.1 ASTM Standards	2-2
	2.2 Industry Standards	2-5
	2.2.1 Renewable Fuels Association	2-5
	2.2.2 Producer & Purchaser Standards	2-6
	2.2.3 Common Storage Terminals	2-6
Section 3	Ethanol Characteristics and Blending Properties and	3-1
	Their Effect on Gasoline Ethanol Blends	
	3.0 Ethanol Characteristics and Blending Properties and	3-2
	Their Effect on Gasoline Ethanol Blends	
	3.1 Water Tolerance	3-2
	3.2 Octane Response Curve	3-3
	3.3 Oxygen Content	3-7
	3.4 Energy Content	3-9
	3.5 Latent Heat of Vaporization	3-11
	3.6 Oxidation Stability	3-11
	3.7 Materials Compatibility and Permeation	3-13
	3.7.1 Materials Compatibility	3-13
	3.7.2 Permeation	3-14
	3.8 Ethanol and Evaporative Emissions Control Canister Operations	3-18
	Section 3 References	3-20

Section 4	Fuel Volatility - Vapor Pressure, Distillation Properties, Vapor Lock Protection Class, and Driveability Index	4-1
4.0	Fuel Volatility - Vapor Pressure, Distillation Properties, Vapor Lock Protection Class, and Driveability Index	4-2
4.1	Vapor Pressure	4-3
4.2	Distillation Properties	4-5
4.3	Vapor Lock Protection Class	4-7
4.4	Driveability Index	4-9
	Section 4 References	4-14
Section 5	World-Wide Fuel Charter	5-1
5.0	World-Wide Fuel Charter	5-2
	Section 5 References	5-7
Section 6	Regulating Entities	6-1
6.0	Regulating Entities	6-2
6.1	Federal Regulatory Agencies and Departments	6-2
6.1.1	U.S. Environmental Protection Agency (EPA)	6-2
6.1.2	U.S. Department of Energy (DOE)	6-4
6.1.3	Federal Trade Commission (FTC)	6-4
6.2	State Regulatory Agencies and Departments	6-4
6.2.1	State Fuel Quality Programs	6-4
6.2.2	State Environmental Agencies/Departments	6-6
6.3	Counties and Municipalities	6-7
6.4	National Conference on Weights and Measures	6-8
	Section 6 References	6-9
Section 7	E-85 Issues	
7.0	E-85 Issues	7-2
	Section 7 References	7-8

Section 8	E diesel™ Issues	8-1
	8.0 E diesel™ Issues	8-2
	Section 8 References	8-11
Section 9	Fuel Cell Issues	9-1
	9.0 Fuel Cell Issues	9-2
Section 10	Glossary of Acronyms and Commonly Used Terms	10-1

TABLES

Table 2-1	ASTM D 4806 Performance Requirements	2-2
Table 3-1	Octane Response with Ethanol	3-6
Table 3-2	MON and RON Increases - 10v% Ethanol	3-7
Table 3-3	Factors that Influence Fuel Economy of Individual Vehicles	3-9
Table 3-4	Energy Content of Oxygenate Blends (when blended with 114,000 btu/gal base fuel)	3-10
Table 3-5	Average Permeation Rate	3-16
Table 4-1	Effects of Gasoline Volatility on Vehicle Performance	4-2
Table 4-2	Estimated Vapor Pressure of Gasoline Ethanol Blend from Adding 10v% Ethanol	4-4
Table 4-3	Vapor Lock Protection Class Requirements	4-8
Table 4-4	ASTM D 4814 Gasoline Volatility Requirements	4-13
Table 7-1	Requirements for Fuel Ethanol (Ed75-Ed85)	7-3
Table 7-2	Comparison of E-85 Properties to Gasoline Properties	7-6
Table 8-1	Comparison of Typical Properties-No. 2 Diesel to E diesel™	8-3

FIGURES

Figure 3-1	Water Tolerance of Gasoline/Fuel Ethanol Blends	3-2
Figure 3-2	Blending Octane Value of Common Oxygenates	3-4
Figure 3-3	Octane Value of Common Oxygenates	3-5
Figure 4-1	Seasonal Blends Vaporization Characteristics	4-3
Figure 4-2	Importance of Proper Distillation	4-6
Figure 4-3	Effects of Fuel Oxygenates on Distillation Curve	4-7

Section 1

Background, Introduction, & Summary of Recommendations

1.0 Introduction, Background, & Summary of Recommendations

The Office of Energy Efficiency and Renewable Energy (EERE) in the U.S. Department of Energy (DOE) is responsible for technology development and the analysis of technical, regulatory, and market factors relevant to the increased use of biomass-based fuels, electricity, and chemical feedstocks and products. Oak Ridge National Laboratory (ORNL) is supporting the EERE in the analysis of current and future ethanol demand for the transportation fuels market. Downstream Alternatives, Inc. (DAI) was retained to provide technical expertise specifically related to ethanol transportation, distribution, and marketing issues as well as certain technical and fuel specification issues.

The DOE is interested in these issues because it is engaged in research and development work on cellulosic ethanol development. Understanding the infrastructure development necessary for an expanded ethanol industry, as well as any technical challenges, is an important part of this work.

This document is part of a series of project deliverables prepared for ORNL under Subcontract No. 4500010570.

A number of transportation fuel specifications and fuel property issues can impact the operational practicality, and the economics, of using ethanol in various transportation fuel applications. Ethanol's unique blending properties affect compliance with various fuel related parameters in both positive and negative ways. This compendium was developed to serve as a general information reference tool to the ethanol industry, related industries, and those in local, state, and federal government who may need to familiarize themselves with such issues.

While the majority of issues identified pertain to low level gasoline ethanol blends of 10 volume percent or less, developing issues with E diesel™, E-85, and ethanol in fuel cell applications are also discussed. In those cases where operational changes, research recommendations, or public policy changes could help address the challenges of a certain issue, such items are discussed. A summary of the recommendations resulting from this work are recapped below by applicable report section.

Summary of Recommendations

Section 3: Ethanol Characteristics and Blending Properties and Their Effect on Gasoline Ethanol Blends

3.6 Oxidation Stability/Recommendation: *Because the oxidation stability of gasoline ethanol blends in typical U.S. gasolines has not been thoroughly studied, further research is warranted. The same applies to E-85. It is recommended that one of the National Laboratories, a university, or a qualified contractor undertake research to determine the effect of ethanol on the storage stability of both E-10 and E-85 blends as well as on E-95, since denatured ethanol may sometimes be stored for extended periods.*

3.8 Ethanol and Evaporative Emissions Control Canister Operations/Recommendation: *Either through a technical literature search or communication with the manufacturers of the activated carbon and canisters it should be determined that the activated carbon and pore size being used are adequate to address proper adsorption and desorption rates of the evaporative emissions from gasoline ethanol blends. If this cannot be verified, research should be undertaken to determine what steps, if any, need to be taken to ensure proper operation of the evaporative emissions control system when operating on gasoline ethanol blends. Since the automakers emission certify their Flexible Fueled Vehicles (FFVs) on E-10, a review of their evaporative control systems approach might be beneficial. Similar activated carbon systems are employed in various vapor control systems throughout the petroleum distribution system (e.g., Stage I and Stage II vapor recovery). Circumstances in this application are similar and any investigation should probably include such stationary applications.*

Section 4: Fuel Volatility - Vapor Pressure, Distillation Properties, Vapor Lock Protection Class, and Driveability Index

4.1 Vapor Pressure/Recommendation: *Given that no other researchers have found an effective vapor pressure reducing additive it is unlikely that additional research would be successful. However, it might be worthwhile to at least survey some researchers to determine if they believe some other approach to researching this issue could prove fruitful.*

Section 5: World-Wide Fuel Charter

***Recommendations:** The various U.S. government agencies, as well as their counterparts in other countries, need to initiate a dialogue with the auto manufacturers concerning the World-Wide Fuel Charter and global fuels harmonization initiatives. The auto manufacturers need to be made acutely aware of various policies and initiatives that would result in changes to existing and future transportation fuels. When the WWFC is in contrast with public policy objectives, those issues need to be thoroughly discussed to determine if more suitable specifications and text can be utilized in the WWFC. Similarly, this will give the automakers an avenue to explain, in detail, why certain aspects of the WWFC seem to contradict some energy related public policy objectives.*

Section 8: E diesel™ Issues

***Recommendations:** Unresolved technical issues and EPA health effects testing will be expensive and also require significant personnel resources. The DOE, through its National Renewable Energy Laboratory (NREL), was instrumental in bringing stakeholders together to form the E diesel™ Consortium and also covered the expenses of several initial meetings and conference calls. While the consortium expects to pool resources to begin to address the many open technical issues, it is doubtful that required resources could be provided solely by the members of the E diesel™ Consortium. Based on this, the following recommendations are offered:*

- *The DOE, either directly and/or through NREL, should continue to participate in the E diesel™ Consortium. This provides the necessary information flow between industry stakeholders and government.*
- *To the extent possible, the National Laboratories should undertake whatever portion of the necessary testing that is within their capabilities.*

- *If the DOE wishes to see E diesel™ commercialized, more dialogue between the Department and the engine manufacturers would be beneficial.*
- *To the extent possible, and where industry is prepared to match funding, DOE should continue to look for areas to fund worthwhile research projects to address the many unresolved technical issues associated with E diesel™.*

Section 9: Fuel Cell Issues

***Recommendations:** The development of cellulosic derived ethanol will overcome one hurdle for ethanol, supply availability. If transportation fuel cells gradually replace IC engines, likely in the same time frame cellulosic ethanol production will increase, it will be important that ethanol plays a role as a hydrogen carrier for fuel cells.*

Research with multifuel reformers and an ethanol specific reformer needs to continue. Where possible, DOE should pursue opportunities with industry to further such technologies. Additionally, the EERE should closely coordinate efforts between its Biomass, Freedom Cars and Vehicle Technologies, and Hydrogen, Fuel Cells and Infrastructure Technologies programs to ensure that cellulosic ethanol will have a role in the fuel cell fuels market.

Section 2
Ethanol Quality Issues

2.0 Ethanol Quality Issues

The majority of fuel grade ethanol is used in low level gasoline ethanol blends such as E-10. However, it is also used in E diesel™ and E-85 and is being considered for use as a fuel for fuel cell applications.

Regardless of its use, the quality of fuel grade ethanol is very important. There are various industry guidelines and, in some cases, state laws that set the specification and property limits for fuel grade ethanol.

2.1 ASTM Standards

The primary industry standard for fuel grade ethanol is ASTM D 4806 “*Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark Ignition Engine Fuel.*”

Most petroleum companies and gasoline blenders require that, at a minimum, the fuel grade ethanol they purchase meet the specifications set forth in ASTM D 4806. Ethanol producers usually have similar requirements for product exchanges with other producers. The following table lists the primary fuel grade ethanol properties specified in ASTM D 4806. Where applicable the ASTM test method for determining a property is listed.

Table 2-1 ASTM D 4806 Performance Requirements		
Property	Specification	ASTM Test Method
• Ethanol volume %, min	92.1	D 5501
• Methanol, volume %, max	0.5	
• Solvent-washed gum, mg/100 ml max	5.0	D 381
• Water content, volume %, max	1.0	E 203
• Denaturant content, volume %, min	1.96	
volume %, max	4.76	
• Inorganic Chloride content, mass ppm (mg/L) max	40	(32) D 512
• Copper content, mg/kg, max	0.1	D1688
• Acidity (as acetic acid CH ₃ COOH), mass percent (mg/L), max	0.007	(56) D1613
• pH	6.5-9.0	D 6423
• Appearance - visibly free of suspended or precipitated contaminants (clear & bright)		

The importance of the properties specified in the above table is discussed below:

Ethanol Volume % Minimum: Specifying the minimum ethanol content is essential to minimize the presence of impurities. The minimum ethanol content of denatured ethanol plus the denaturant make up at least 96.86% of the total volume thereby limiting impurities to under 3%. Impurities typically found in commercially produced fuel ethanol include such compounds as methanol and fusel oils such as amyl and isoamyl alcohols.

Methanol Volume % Maximum: The maximum methanol content of ethanol is limited because methanol, in higher quantities, is an unacceptable contaminant. Methanol increases the blending vapor pressure of ethanol, is less tolerant to water, and may be aggressive to certain metals and elastomers found in automobile fuel systems and retail fuel dispensing equipment.

Solvent-Washed Gum: Solvent-washed gum can contribute to fuel system deposits. The impact of solvent washed gums for ethanol, in modern engines, is not well defined. However, the test detects high boiling, heptane insoluble impurities and helps lower solvent gum levels in the final fuel blend.

Water Content: Blends of fuel ethanol and gasoline have a limited solvency for water. This solvency can be affected by the ethanol content, temperature, and aromatic content of the gasoline in the blend. A typical gasoline ethanol blend could keep about 0.5 v% water in suspension at 60°F (15.56°C). Higher water levels result in blend stratification and ultimately, phase separation. The denser phase of the separation will contain water, ethanol, and a small amount of hydrocarbons and is unsuitable for internal combustion engines. Consequently providing an ethanol with a low level of water (less than 1.0 v%, and preferably lower) is very important.

Denaturant Content: The Bureau of Alcohol, Tobacco, and Firearms (BATF) requires that fuel grade ethanol be denatured to avoid payment of the beverage alcohol tax. The BATF permits the use of several denaturants and specifies the volume range of denaturant to be added. However, the BATF regulations

are designed simply to render the ethanol non-potable. Certain denaturants permitted by BATF may not be suitable for fuel grade ethanol from the standpoint of fuel quality. For instance, ketones such as 4-methyl pentanone (methyl isobutyl ketone) tend to degrade fuel stability. Kerosene could contribute to piston scuffing. Because of the above, ASTM D 4806 permits only hydrocarbons in the gasoline boiling range to be used as denaturants, and lists certain materials that are not permitted as denaturants under any circumstance.

Inorganic Chloride: The maximum inorganic chloride content is critical because even low levels of chloride ions are corrosive to many metals.

Copper Content: Copper is a catalyst for oxidation of hydrocarbons at low temperatures. It contributes to a faster rate of gum formation. Its presence in fuel ethanol, and gasoline, must therefore be kept to very low levels.

Acidity: Low molecular weight organic acids such as acetic acid (CH_3COOH) are corrosive to certain metals and must be kept to low levels.

pHe: The pHe test procedure was originally developed by General Motors Corporation. A modification of the test procedure and a pHe standard was later adopted by ASTM. Very low levels of highly acidic compounds in ethanol may not always be detected by other test procedures. The pHe test, and standard, were adopted to address this issue. Fuel grade ethanol with a pHe below 6.5 may contribute to failure in fuel pumps and fuel injectors due to corrosive wear. If the pHe is above 9.0, it may have a deleterious effect on plastic parts in the fuel system. These effects are more pronounced on high level blends such as E-85. Any adverse effects are much less at lower blend levels such as E-10.

Sulfur Content: California has adopted very stringent maximum sulfur levels for their gasoline while the remainder of the country has also adopted very strict gasoline sulfur standards, although they are more

lenient than California. As a result, ASTM D 4806 now incorporates language to address these standards. The California requirement also limits the level of other components in ethanol and specifies certain properties for the denaturant. The California requirement limits the sulfur level of ethanol to a maximum of 10 ppm. They also require a 0.06 v% maximum limit for benzene, 0.50 v% maximum limit for olefins, and 1.70 v% maximum limit for aromatics. California requires that denaturants used in fuel ethanol not exceed the maximum content limits of 1.1 v% for benzene, 10.0 v% for olefins, and 35.0v% for aromatics. California standards allow higher amounts of these components if the supplier can assure that the denaturant will be used at less than the 4.76 v%, and the specified limits for denatured fuel ethanol are still met. At the federal level, denatured ethanol must not exceed a maximum sulfur content of 30 ppm, beginning January 1, 2004.

NOTE: ASTM D 4806 and other ASTM standards are available from:

ASTM
100 Bar Harbor Drive
W. Conshohocken, PA 19428-2959
Publication orders • phone (610) 832-9585 • fax (610) 832-9555

2.2 Industry Standards

ASTM D 4806 serves as the industry standard for fuel ethanol but it is considered a minimum standard by some. Others may have more stringent requirements as described below.

2.2.1 Renewable Fuels Association

The Renewable Fuels Association (RFA) is the industry trade association for the domestic fuel ethanol industry. It prepares various guidelines and recommended practices for its members, their customers, and others.

RFA Publication #960501 *Fuel Ethanol Industry Guideline Specifications and Procedures (Revised May 2002)* is the primary guideline for ethanol properties for the domestic fuel industry. The RFA, through Publication #960501, recommends that all of its member companies adhere to ASTM D 4806 but includes additive recommendations as well.

The RFA recommends that a corrosion inhibitor be added to all fuel grade ethanol at a treat rate such that gasoline ethanol blends will provide corrosion protection comparable to other available engine fuels.

While the RFA does not endorse a specific corrosion inhibitor, they have established criteria for what the additive should achieve. Specifically the guideline calls for ethanol to be added to an E rated gasoline (NACE Standard Test Method TM-01-77). The additive, when blended at the recommended treat rate, must raise the NACE rating to B+ or better.

On July 23, 2002, the RFA Board of Directors also voted to recommend that their ethanol producing members meet the California fuel ethanol requirements for maximum sulfur, benzene, aromatics, and olefin content on a nationwide basis. Future editions of RFA Publication # 960501 will incorporate this recommendation.

Copies of RFA Publication #960501 and other RFA documents can be obtained at www.ethanolrfa.org.

2.2.2 Producer & Purchaser Standards

Companies that produce ethanol, as well as those that purchase ethanol, may develop their own standards which may be more stringent than ASTM or RFA guidelines. Such standards may be used for sales purchases or exchanges.

2.2.3 Common Storage Terminals

Some terminal operators provide common storage for fuel ethanol at their terminals. Because several ethanol producers are commingling product in the same tank, these terminal operators will sometimes adopt specifications that are slightly more stringent than ASTM to provide a compliance margin for the commingled ethanol.

In general, specifications on fuel grade ethanol are beneficial to the industry and improve product quality. It is, however, important that standards not vary widely among states or regions since to do so could fragment the fungibility of ethanol.

Section 3

**Ethanol Characteristics and Blending Properties
and Their Effect on Gasoline Ethanol Blends**

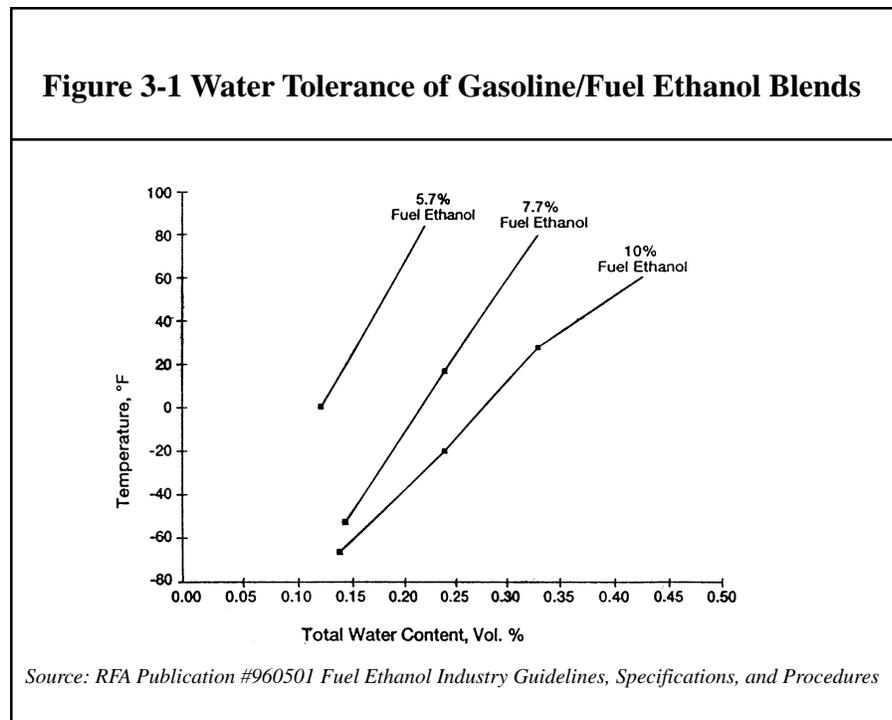
3.0 Ethanol Characteristics and Blending Properties and Their Effect on Gasoline Ethanol Blends

While some of the properties and characteristics of denatured ethanol are similar to gasoline, others are not. Ethanol's unique properties and handling characteristics may require special handling procedures. It may also, in some cases, necessitate changes in the base gasoline into which it is blended. In addition, certain properties of gasoline ethanol blends may present unique considerations for the automobile manufacturers. The most important of these issues is discussed below.

3.1 Water Tolerance

Ethanol has an affinity for moisture and is completely soluble in water. This is one of the reasons that pipelines have been reluctant to ship ethanol, or gasoline ethanol blends, on a commercial scale. If the ethanol, or gasoline ethanol blend, picks up water in the pipeline it could "phase separate" resulting in off-specification product and potential contamination of other products interfaced with the ethanol shipment. Consequently, ethanol is shipped to finished product distribution terminals by other modes of transport and blended with the gasoline as it is loaded into the transport truck for delivery to retail.

A gasoline ethanol blend containing 10 v% ethanol can typically contain up to 0.5 v% water at 60°F before phase separation occurs. Lesser amounts of water can induce separation at lower temperatures. For instance, at 0°F, this same blend would phase separate from a water content of 0.3 v%. The base composition of the gasoline can alter the phase separation point



slightly. Also lower blend levels of ethanol such as 5.7 v% or 7.7 v% tolerate less water. Figure 3-1 depicts the water tolerance levels of the three ethanol content levels most commonly used in gasoline ethanol blends.

At the retail level, precautions must be taken to eliminate any moisture from the underground storage tanks prior to converting to gasoline ethanol blends. Both the American Petroleum Institute (API)⁽¹⁾ and the Renewable Fuels Association (RFA)⁽²⁾⁽³⁾ offer guides on the preparatory action and ongoing steps necessary for a proper ethanol blending program.

Once the underground tank system is properly prepared, water is seldom a problem. This is because the ethanol in the blend will eliminate trace amounts of moisture from the system.

Phase separation of a gasoline ethanol blend in an automobile is rare, but can occur. When it does occur, it is usually a result of water being present in the tank.

In the past, concerns have been expressed about the possibility of a gasoline ethanol absorbing enough moisture from the atmosphere to induce phase separation. However, to put this in perspective, it would take roughly four teaspoons of water in each gallon of gasoline ethanol blend to induce phase separation. To absorb that much moisture from the atmosphere (at a relative humidity of 70%) would take hundreds of days. ⁽⁴⁾

The water tolerance of ethanol and gasoline ethanol blends requires unique handling procedures. However these procedures are well established and present no major obstacles to ethanol's commercial viability.

3.2 Octane Response Curve

One of ethanol's positive attributes, and one of the main reasons it is blended into gasoline, is its ability to increase the octane of the gasoline to which it is added.

Gasolines are most commonly rated based on their Antiknock Index (AKI), a measure of octane quality. The AKI is a measure of a fuel's ability to resist engine knock (ping). The AKI of a motor fuel is the average of the Research Octane Number (RON) and Motor Octane Number (MON) or $(R+M)/2$.

This is also the number displayed on the black and yellow octane decal posted on the gasoline pump. Optimum performance and fuel economy is achieved when the AKI of a fuel is adequate for the engine in which it is combusted. There is no advantage in using gasoline of a higher AKI than the engine requires to operate knock-free.

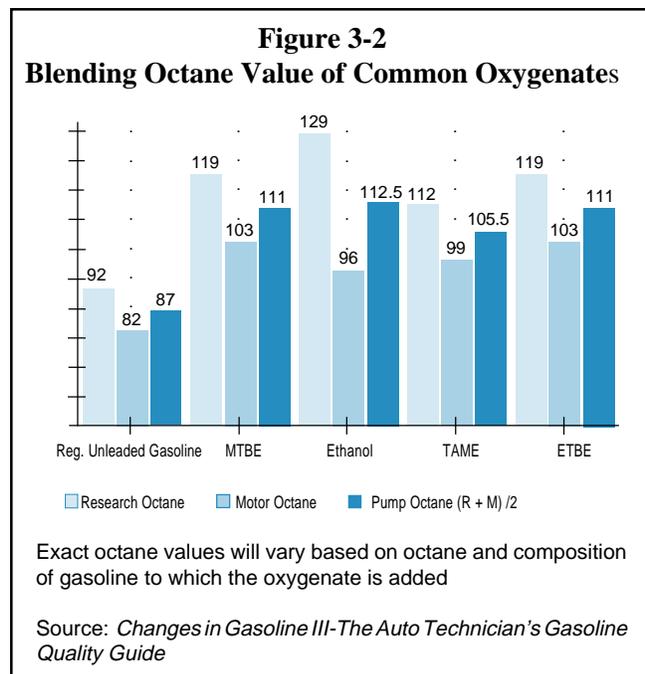
The RON and MON of fuels are measured by recognized laboratory engine test methods. Results of these tests may generally be translated into approximate field performance.

In general, the RON affects low to medium speed knock and engine run-on or dieseling. If the Research Octane Number is too low, the driver could experience low speed knock and engine run-on after the engine is shut off.

The MON affects high speed and part-throttle knock. If the MON is too low, the driver could experience engine knock during periods of power acceleration such as passing vehicles or climbing hills.

The antiknock performance of a fuel, in some vehicles, may be best represented by the RON, while in others it may relate best to the MON. Extensive studies indicate that, on balance, gasoline antiknock performance is best related to the average of the Research and Motor Octane Numbers, or $(R+M)/2$. This formula is continuously reviewed for its accuracy in predicting gasoline performance in new automobiles. Generally speaking, the addition of 10 v% ethanol will increase the octane of the gasoline to which it is added by 2 to 3 $(R+M)/2$ octane numbers. However, the actual octane increase is dependent upon the octane of the base fuel and, to a lesser degree, its composition. The octane increase is more pronounced for research octane than for motor octane.

Ethanol's blending octane value (BOV) typically cited in various literature (3) (4) is 129 for Research Octane Number (RON) and 96 for Motor Octane Number

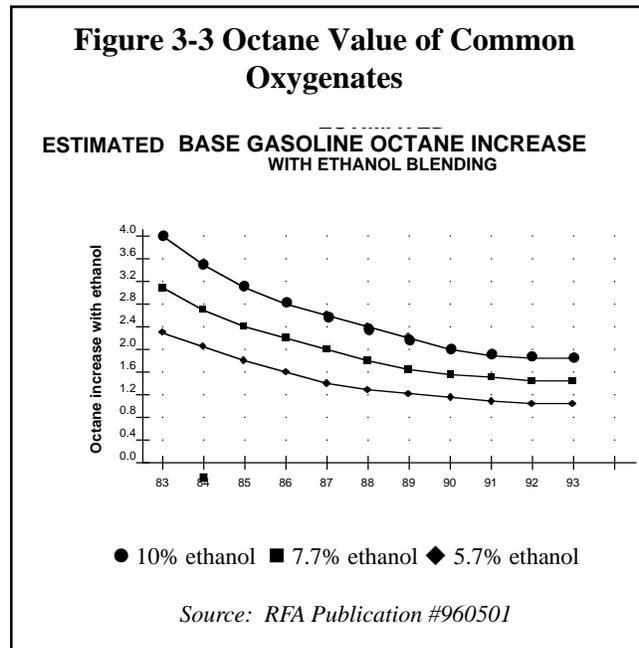


(MON) resulting in an Antiknock Index, or blending octane of $112.5 (R+M)/2$. Figure 3-2 compares the BOV of ethanol to that of MTBE and TAME, both commonly used oxygenates.

Until recently, ethanol was almost always added to gasoline at the 10 volume percent level. However, in the past few years, environmentally driven fuel specifications and changes in motor fuel excise tax laws have also encouraged ethanol blending at 5.7 v% and 7.7 v%.

At the 7.7 v% level, the octane increase typically ranges from 1.5 to 2.5 octane numbers. At the 5.7 v% level, the increase is typically 1.0 to 1.5 octane numbers. Figure 3-3 depicts the octane response, at the three common ethanol blend levels, for various octane level base fuels.

The composition of the base fuel also determines, to a lesser degree, the BOV of ethanol. For



instance, previous tests have determined that the $(R+M)/2$ BOV of 10% ethanol in alkylate is 126, while in Light Straight Run Gasoline it is in the 143 to 147 $(R+M)/2$ range. The octane response of blending 10 v% ethanol with various refinery components is listed in Table 3-1.

As can be seen from the BOV's in the table, the octane value of ethanol will depend on the fuel components an individual refiner is working with.

Another issue is that of octane sensitivity.

Octane sensitivity is the difference between the

RON and the MON and is defined by $RON - MON = \text{Sensitivity}$. It is desirable to have as low an octane sensitivity as possible, with 10 or below being desirable for unleaded regular. As an example an 87 $(R+M)/2$ octane gasoline might have a RON of 92 and a MON of 82. This results in an $(R+M)/2$ of 87 and a sensitivity of 10. However, a gasoline with a 93 RON and a 81 MON would also be 87 $(R+M)/2$ but would have a sensitivity of 12. ASTM guidelines⁽⁵⁾ suggest that unleaded fuel having an AKI of 87 or higher have a minimum MON of 82 in order to protect those vehicles that are sensitive to MON.

Table 3-1 Octane Response with Ethanol

Refining Component	RON	MON	(R+M)/2
Alkylate	96.5	93.5	95.0
10% EtOH	101.9	94.3	98.1
EtOH BV*	151.0	102.0	126.5
Light St. Run (Refinery A)	72.3	70.0	71.2
10% EtOH	80.4	77.1	78.8
EtOH BV	153.0	141.0	147.0
Light St. Run (Refinery B)	69.8	67.8	68.8
10% EtOH	77.6	74.8	76.2
EtOH BV	148.0	139.0	143.5
Cat Cracked (Refinaery A)	60.7	59.5	60.1
10% EtOH	70.6	68.4	69.5
EtOH BV	160.0	149.0	154.5
Cat Cracked (Refinery B)	87.6	78.9	83.3
10% EtOH	91.7	80.9	86.3
EtOH BV	129.0	99.0	114.0
Reformate (Refinery A)	94.0	83.2	88.6
10% EtOH	96.9	85.4	91.2
EtOH BV	123.0	105.0	114.0
Reformate (Refinery B)	84.1	76.8	80.5
10% EtOH	89.5	80.6	85.1
EtOH BV	138.0	115.0	126.5

*Blending Value
Source: ADM

However, there is not a requirement for a higher MON for premium grades. As an example, one 92 octane premium could have a MON of 82 and a RON of 102 while another could have a MON of 84 and a RON of 100. While both of the aforementioned premium grades are 92 (R+M)/2, the latter example would generally be considered of higher octane quality due to its higher MON and lower octane sensitivity. This is especially true in cars sensitive to MON.

Since a larger portion of the octane response of blending ethanol comes from the increase in RON, this could be an issue for refiners who are struggling to maintain MON. A refiner with an 84.5 (R+M)/2 basestock with a RON of 89 and a MON of 80 would achieve 87.3 (R+M)/2 by blending 10 v% ethanol. But using ethanol's commonly accepted BOVs the MON would be only 81.6, falling short of the recommended 82 MON. This calculation is demonstrated in the Table 3-2.

Table 3-2 MON and RON Increases - 10 v% Ethanol					
	BOV Gasoline	BOV 10 v% etoh	Octane Contribution Gasoline	Octane Contribution Ethanol	Total Octane Value
MON	80	96	72	9.6	81.6
RON	89	129	80.1	12.9	93.0
(R+M)/2	84.5	112.5	76.05	11.25	87.3

As can be seen in the above table, the AKI of the base gasoline is increased by 2.8 numbers by adding 10 v% ethanol, but the increase in MON is only 1.6 over the base fuel while the increase in RON is 4.0.

So while octane, or AKI, is often cited, the actual calculation for the refiner is a little more detailed because two fuels of the same octane, as defined by (R+M)/2, may not truly be of the same octane quality.

3.3 Oxygen Content

Undenatured ethanol is 34.7 wt% oxygen⁽⁶⁾. While denatured ethanol is typically 33.0 wt% oxygen. ⁽²⁾ In addition to its use as an octane enhancer, ethanol is often used to comply with minimum and/or average oxygen content requirements. These oxygen requirements are applicable in CO non-attainment areas (oxyfuel programs) and certain ozone non-attainment areas (reformulated gasoline programs) as defined in the 1990 Clean Air Act Amendments and subsequent EPA rulemakings and guidance documents.

Until the early 1990s, ethanol was usually blended into gasoline at a concentration of 10v% of the final blend. With the advent of oxygenated fuel and reformulated gasoline (RFG) programs, some companies blend at lower levels to achieve targeted oxygen levels. Due to differences in gasoline density compared to ethanol density, the most popular blend ratios yield the following approximate oxygen contents. ⁽²⁾

<u>Volume % Denatured Ethanol in Fuel</u>	<u>Oxygen Content</u>
10.0% by volume	3.5% by weight
7.7 % by volume	2.7% by weight
5.7% by volume	2.0% by weight

The final oxygen content of a gasoline/ethanol blend is affected by the purity of the ethanol, its denaturant level and moisture content, as well as the specific gravity of the gasoline to which it is being added. The U.S. Environmental Protection Agency (EPA) has issued guidance documents on compliance with oxygenated fuel and reformulated gasoline programs. Because of the above mentioned variables the latest applicable EPA guidance documents should be referred to if utilizing ethanol to comply with the oxygen standards of a mandatory oxygenated fuels or RFG program.

It should also be noted that when blending gasoline/ethanol blends under the "gasohol waiver"⁽⁷⁾ that an oxygenate free base gasoline must be used. EPA has, however, ruled that gasolines containing up to 2 v% MTBE, due to inadvertent commingling or contamination, may be used as the base fuel for gasoline/ethanol blends containing up to 10% ethanol.

If ethanol is used in combination with other oxygenates (other than 2 v% MTBE) then the "gasohol waiver" is not applicable and the "substantially similar" rule applies. In this case the total oxygen content of the fuel may not exceed 2.7 wt% to meet the "substantially similar" definition.

Older vehicles (pre-computer control) can typically tolerate the 3.5 wt% oxygen level of gasoline ethanol blends containing 10 v% ethanol without any adjustments.⁽⁴⁾

Modern automobiles are equipped with onboard computer control systems. An oxygen sensor, installed in the exhaust manifold, determines (once reaching operating temperature) the content of uncombusted oxygen in the exhaust gas and provides that input to the computer. The computer, in turn, adjusts the fuel flow to compensate for the oxygen content.

The calibration of the vehicle computer system, and authority ranges of the oxygen sensors, are typically designed to identify oxygen levels up to the currently permitted maximum of 3.5 wt% oxygen. Some vehicles may identify and calibrate for higher oxygen levels. If ethanol is to be used at higher blend

levels (i.e., above 10 v%) resulting in higher oxygen levels, it may be necessary to recalibrate some automobiles.

3.4 Energy Content

Ethanol contains less energy than gasoline. Based on lower heating value, the energy content of gasoline typically ranges from 108,500 to 117,000 btu/gal with 114,000 btu/gal providing a fairly representative average. The energy content of neat ethanol is 75,563 btu/gal ⁽⁸⁾ which after denaturing results in an energy content of 77,422 btu/gal. Compared to a gallon of gasoline at 114,000 btu/gal, denatured ethanol contains 36, 578 btu/gal (32.2%) less energy. At the 10 v% blend level, this would equate to 3.21 % less energy for the finished blend. There is a great deal of misunderstanding about the fuel economy (miles per gallon) of various gasolines, especially those containing oxygenates.

There are a number of variables that confound accurate fuel economy measurements in anything short of a controlled test or large well documented fleet study.

Besides fuel related factors, there are a number of vehicle and climate related issues to consider. Vehicle technology, state of tune, ambient temperatures, head winds, road grade, tire pressure, use of air conditioners, and numerous other factors have an impact on fuel economy. Many of those have been documented in testing.

Some examples of various factors that influence fuel economy and their average and maximum effects are listed in the following table.

Table 3-3		
Factors That Influence Fuel Economy of Individual Vehicles		
Factor	Fuel Economy Impact	
	Average	Maximum
Ambient temperature drop from 77°F to 20°F	-5.3%	-13.0%
20 mph head wind	-2.3%	-6.0%
7% road grade	-1.9%	-25.0%
27 mph vs. 20 mph stop and go driving pattern	-10.6%	-15.0%
Aggressive versus easy acceleration	-11.8%	-20.0%
Tire pressure of 15 psi versus 26 psi	-3.3%	

Source: Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide, DAI, 1996

Through the course of a year, gasoline energy content can range from 108,500 btu/gal to 117,000 btu/gal. Winter grades are made more volatile (less dense) to aid in cold start and warm up performance and typically contain 108,500 to 114,000 btu/gallon. Summer grades are of much lower volatility to minimize evaporative emissions and hot start/hot driveability problems. Summer grades will typically contain 113,000 to 117,000 btu/gallon. So the energy content, and therefore fuel economy, can vary 3.4% to 5.0% just based on the energy content of the fuel on a seasonal basis.

In those cases where ethanol is used to meet the oxygen requirement of regulatory programs such as an oxyfuel or reformulated gasoline program, the most appropriate energy content comparison would be to compare ethanol blends to MTBE blends. The following table offers such a comparison.

Table 3-4 Energy Content of Oxygenate Blends (when blended with 114,000 btu/gallon base fuel)			
Oxygenate	Energy content (btu/gal)	<u>Finished blend</u> 2.0 wt.% oxygen btu/gallon	<u>Finished blend</u> 2.7 wt.% oxygen btu/gallon
Ethanol	77,422	111,915	111,183
MTBE	93,500	111,745	110,925

The above table demonstrates that at the same oxygen levels ethanol provides comparable, and in fact, slightly higher energy content than the MTBE blends. For the average consumer driving a vehicle that averages 25 miles per gallon (mpg), the fuel economy penalty of a gasoline oxygenate blend equates to 0.5 to 0.8 mpg compared to the 114,000 btu/gal base fuel. Put another way, a vehicle with a ten gallon tank would have its range reduced from 250 miles to the 242-245 mile range. These differences are not only undetectable by the typical motorist, but are no more of an energy content variation than can be found among fuels that do not contain oxygenates. However, this fuel economy penalty is normally included in computer models that are national or regional in scope because, at these levels, such variations in fuel economy can be important.

3.5 Latent Heat of Vaporization

Latent heat of vaporization is the heat associated with a change from a liquid to a gas at a constant temperature,⁽⁹⁾ also sometimes called heat of vaporization.

Ethanol's heat of vaporization is much higher than gasoline. Gasoline's heat of vaporization is ~ 170 btu/lb. while ethanol's is 390 btu/lb. In brief, it takes more energy (heat) to vaporize a given amount of ethanol than an equivalent amount of gasoline.

Ethanol's high heat of vaporization can be detrimental at low temperatures where it becomes more difficult to vaporize the fuel during cold start. This effect is more pronounced on high blend levels such as E-85. For instance, more gasoline is added to E-85 during the colder months, to provide for vaporization and the blend is technically E-75 in the coldest winter months.

In some circumstances, ethanol's heat of vaporization can be beneficial. As liquid fuel evaporates in the air stream being charged to the engine, a high heat of vaporization cools the air, allowing more mass to be drawn into the cylinder thereby increasing the power produced. The lower charge-air temperature decreases the maximum combustion temperature and in turn the thermal load on the engine.

Ethanol's heat of vaporization has minimal effect on gasoline containing 10 v% ethanol or less. The typical result is that the initial vaporization point of the gasoline may be increased 1°-3°F.

3.6 Oxidation Stability

Oxidation stability, as determined by ASTM D 525 *Test Method for Oxidation Stability of Gasoline (Induction Period Method)* measures an induction period to provide an indication of the resistance of a fuel to form gum in storage. However, such test results can vary markedly from actual field performance due to different storage conditions (e.g., ambient temperature, color of tank and its effect on product temperature).

In the United States, ethanol is typically not added to the gasoline until it is being loaded into the transport truck for delivery to the retail facility. Retail facilities typically turn their inventory very quickly, usually in ten days or less. Consequently, the potential for ethanol to increase the gum formation of gasoline in storage has not been considered a major concern in the U.S. and has not been closely studied.

One detailed study by Petrobras⁽¹⁰⁾ found that the addition of ethanol at levels “from 13 to 25% in volume, tends to increase the gasoline storage instability in terms of gum formation.” These conclusions were, however, based on blend levels higher than those used in the U.S. and also based on storage periods of 8 to 24 weeks. Additionally, the base gasolines used in the tests may have differed from typical gasolines sold in the U.S. Due to the short storage time for a gasoline ethanol blend in the U.S. market, fuel stability should not be a problem. However, should long storage periods ever develop, this could become an issue.

No information on the storage stability of E-85 was found in the literature reviewed.

It should be noted that there may be instances where gasoline ethanol blends may be stored in their blended form for longer periods of time. For instance, some fleet fueling facilities may take several weeks to turn tank inventory over. Similarly, because E-85 is currently a low sales volume product, it could remain in storage for extended periods of time.

Recommendation: *Because the oxidation stability of gasoline ethanol blends in typical U.S. gasolines has not been thoroughly studied, further research is warranted. The same applies to E-85. It is recommended that one of the National Laboratories, a university, or a qualified contractor undertake research to determine the effect of ethanol on the storage stability of both E-10 and E-85 blends as well as on E-95, since denatured ethanol may sometimes be stored for extended periods.*

3.7 Materials Compatibility and Permeation

Materials compatibility and permeation are discussed together because they are, in many ways, related. Vehicle fuel system components consist of a wide variety of materials that can generally be classified as either metals, elastomers, or composites.

Metals can be found in fuel tanks, fuel lines, fuel pumps, fuel regulators, fuel rails, fuel injectors, and, in the case of older vehicles, carburetors. Types of metals used in vehicle fuel systems include aluminum alloy, magnesium alloy, copper, zinc, carbon steel, cartridge brass, and stainless steel.⁽⁴⁾

Elastomers are generally soft rubberlike compounds with typical fuel system uses including fuel lines, fuel pump seals, fuel injector o-rings, and carburetor gaskets. Types of elastomers used include such materials as nitrile butyl rubber, epichlorohydrin copolymer, and fluoroelastomers.⁽⁴⁾

Composite materials consist of two or more physically different materials, which are typically bonded together or laminated, incorporating the properties of both materials. Examples would be multilayer co-extruded fuel tanks or multilayer hoses where, in the latter case, the external gasket of a fuel line might be ethylene acrylic elastomer followed by a carbon fiber liner and with the inside layer (the one with immediate contact with the fuel) being a fluoroelastomer.⁽¹¹⁾

Materials compatibility could be loosely defined as the ability of a material to retain all, or most of its properties, when coming in contact with a specific substance. As an example, if a fluoroelastomer fuel line were tested on a highly aromatic gasoline or gasoline ethanol blend, and retained adequate properties to perform its intended use, it would be said to be compatible for use with those fuels.

Permeation is essentially a measure of the ease with which a fluid, or its vapor, can diffuse through a particular material, or more specifically in this case, the migration of hydrocarbon molecules through any of the materials used in the vehicle fuel system. Even fuel system elastomers and composites which are fuel compatible experience some level of permeation under certain conditions. Permeation is not a concern with fuel system metals.

3.7.1 Materials Compatibility

Historically changes in gasoline have necessitated a corresponding change in fuel system

materials to remain compatible with new fuel composition.⁽¹¹⁾ Additionally improved materials have been incorporated into later model vehicles to achieve even tighter vehicle evaporative emissions standards.⁽¹²⁾

By the early 1980s, alcohols and ethers were introduced into fuels to provide octane as lead was removed from gasoline, thereby requiring changes in some materials used in the fuel system. While there is little empirical evidence that pre-1980 vehicles experienced any major materials compatibility problems on gasoline ethanol blends, there have been anecdotal reports. Tests indicate certain materials in these older vehicles are not as durable, for gasoline ethanol blends use or for even highly aromatic gasolines, as the materials used today.

In 1985 there was a major move to fuel injected systems. The elastomeric components of these fuel systems are, for the most part, made of fluoroelastomers and therefore compatible with ethanol, higher aromatic level gasoline, and other oxygenates (e.g., ethers). Auto manufacturers and the fuel system component suppliers long ago identified the appropriate materials to use to ensure compatibility with today's gasoline formulations.

Similarly there have been no major concerns about compatibility with metals used in the vehicle fuel system. The auto manufacturers have indicated they have no major concerns about the metals in their vehicle fuel systems providing certain quality conditions are met for the ethanol used in gasoline. Those conditions are that the ethanol content of the gasoline (in the U.S.) not exceed 10 v% and that the ethanol used in the blend meet the standards set forth in ASTM D 4806 *Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel* and provided that the resulting blend has corrosion ratings comparable to other commercially available gasolines.

3.7.2 Permeation

While materials compatibility issues have been addressed, permeation is a more complex issue. The 1990 Clean Air Act Amendments required that enhanced evaporative emissions controls be phased in between 1995 and 1999. This has resulted in the use of fuel system materials that are more resistant

to permeation by various fuel components.⁽¹²⁾ Even more stringent requirements were adopted in EPA's Tier II Rulemaking⁽¹³⁾ which require not only lower evaporative emissions but implement steps to address the potential that alcohol fuels could increase permeability. Specifically, Tier II rules require that the aging methods used by manufacturers to develop service accumulation (aging) of fuel system materials now include the use of alcohol fuels.

It has been reasonably well established that ethanol can increase the permeation rate of a number of elastomeric materials. This is a result of ethanol being a polar compound while many elastomers and plastics are also polar (e.g., nylon). Ethanol is also a smaller molecule than typical hydrocarbons. This too may contribute to increased permeation of some materials.

SAE has two primary guidance documents for this topic. They are *SAE J 30 Fuel and Oil Hoses* and *SAE J1737 Test Procedure to Determine the Hydrocarbon Losses from Fuel Tubes, Hoses, Fittings, and Fuel Line Assemblies by Recirculation*. To help the reader understand this topic better, the following section is excerpted from section 3.4.2 of SAE J 1737.

“ 3.4.2 Type of Fuel-Alcohol-blend fuels have been used to evaluate materials for potential use in fuel and emissions applications. The effect of such blends on specific materials and composites of more than one material can be significant. For this reason, the test fuel used should be representative of what is likely to be actually encountered in the field. Also, if any comparisons among materials in the area of permeation resistance are ever made, the test fuel used must be as much the same as possible. Typical fuels used in this test are alcohol blends between 5% and 25%. The basic test fuel for use with this procedure should be CM15; with CE10, (ASTM Ref. Fuel C and 10% Ethanol by volume) used a second test fuel; refer also to 5.1, 7.5, and SAE J11681).

Permeation is a result of the solubility and diffusivity of a fluid in a material. Therefore, fuel permeation is affected by the solubility of a given fuel constituent in a given fuel containment material. This solubility effect can be readily observed by measuring the volume swell of a given material when exposed to a specific type of fuel. In many cases, when comparing two different materials that do not have a plasticizer, the greater the swell, the more easily the fuel is dissolved into the material; the resulting permeation rate will then be higher. In other cases, differences in diffusion will cause permeation to be different from predictions based on solubility alone.

Fuel constituents can be broadly classified in two ways: as polar/non-polar and as solvents/co-solvents. Polar or non-polar types will mix readily with their own kind but not with their opposites. Co-solvents permit polar and non-polar solvents to mix. The majority of hydrocarbon compounds in fuel are non-polar. Methanol is one of the most strongly polar fuel constituents. Aromatic hydrocarbons are co-solvents. Their presence is essential for methanol to mix in gasoline.

Plastic and elastomeric materials can also be broadly classified as polar and non-polar. For example, Polyethylene is non-polar, Nylon is polar. Therefore, gasoline (a primary non-polar solvent) tends to permeate polyethylene readily. However, Polyethylene is quite resistant to permeation of pure methanol. The opposite is true for Nylon which is permeated by methanol much more readily than gasoline.

The behavior of mixtures of gasoline is non-ideal in that the resulting properties or effects are not a linear relationship between the effects measured in a pure sample of either liquid. Gasoline/Methanol mixtures tend to produce much greater effects on materials at a methanol concentration of at between 5% and 60%. If one is designing a fuel system for minimum permeation, it is essential to know what fuel mixtures will be encountered.”

Published permeation rates show a wide range of values for various vehicle fuel system materials on gasoline containing 10 v% ethanol, ranging from a 40% decrease to an 838% increase. The following table is from SAE Paper # 920163 *Fuel-Alcohol Permeation Rates of Fluoroelastomers Fluoroplastics, and Other Fuel Resistant Materials* and illustrates this variation.

Table 3-5 Average Permeation Rate			
Permeation rates mathematically normalized to 1 mm thickness (g x mm)/(m ² x day)			
<u>Material</u>	<u>Fuel C</u>	<u>10% Ethanol</u>	<u>% Increase</u>
NBR (33% ACN)	669.00	1028.00	54
FVMQ *Fluorosilicone)	455.00	584.00	28
HNBR (44% ACN)	230.00	553.00	140
Nylon 12	5.50	24.00	336
FKM GLT (65% F)	2.60	14.00	438
FKM GFLT (67% F)	1.80	6.50	261
FKM A200 (66% F)	0.80	7.50	838
FKM B70 (66% F)	0.80	6.70	738
FKM B200 (68% F)	0.70	4.10	486
FKM GF (70% F)	0.70	1.10	57
PFA 1000LP	0.10	0.03	-40
FEP 1000L	0.03	0.03	0
ETFE 1000LZ	0.03	0.10	67

NOTE: There are three typical units of permeation measurement utilized by industry. They are:

Grams/Day: For a vehicle, or complex components or system it is most practical to express permeation measurements in grams per day.

Grams/Meter/Day: When the specimen being tested is a tube or hose, the amount of permeation is expressed as the amount of emissions per unit length and per unit of time.

Grams/Meter²/Day: For simple parts such as tubes and hoses, the permeation rate can also be expressed in measurements of grams per unit of area per day. By including unit area in the measurement, the actual size of the part is eliminated as a factor. When expressed in this manner, the area is the area of the part, component, or material in actual contact with (wetted by) the fuel.

The permeation effects of ethanol is a very complex subject complicated by several factors, First, methanol is often used as the alcohol in the test fuel, especially in older research. It is then referenced to as alcohol and the results then misinterpreted to apply to ethanol which tends to have lower permeation rates than methanol. Secondly, not all tests are done in the same manner. Some tests are done by the ASTM E96 procedure (Thwing-Albert cup method). Others are done by the procedure used in SAE J 30 (at 30.6.12) which uses a length of hose plugged at one end and sealed to a reservoir. Other tests are performed using SHED[†] or mini-SHED procedures. Further complicating matters is that even if exact permeation differences were known, there is no information source to identify the content of these materials currently in use in the existing vehicle population. This makes it extremely difficult to quantify any resulting total evaporative emissions increase.

The Coordinating Research Council (CRC) is in the process of studying this matter in greater detail.⁽¹⁴⁾ The CRC research project will essentially place the complete vehicle fuel system (removed from the vehicle) in a SHED and compare the total evaporative emissions of non-oxygenated fuel, an MTBE blend, and a gasoline ethanol blend. This test will include the fuel systems from ten vehicles ranging from model years 1978 to 2001. This program may help more clearly define the total impact of ethanol permeation across the entire vehicle, at least for the vehicles studied.

However, even with what will hopefully be more accurate permeation rates and resulting evaporative emissions differences, it will be difficult to apply these rates across the vehicle population since the exact elastomers and composites used in each vehicle model year and make are not well documented.

[†] SHED is the acronym for Sealed Housing for Emissions Determination, the current industry procedure for measurement of vehicle evaporative emissions.

Fortunately, the manufacturers of elastomeric materials have long recognized that they must offer materials that are compatible with, and resist increased permeation from, gasolines containing ethanol. For instance, DuPont Dow Elastomers LLC has studied this issue for a number of years and has presented papers ⁽¹⁵⁾⁽¹⁶⁾ identifying specific elastomers to minimize materials compatibility problems and permeation rates when exposed to gasoline ethanol blends.

Numerous other organizations have presented papers on their research in this area. The chemistry of developing appropriate materials is well understood, and under existing regulations will continue to be incorporated into new vehicle fuel systems.

3.8 Ethanol and Evaporative Emissions Control Canister Operations

Automobile fuel systems are equipped with devices to control evaporative emissions. These systems include an evaporative emissions control canister which captures evaporative emissions from the fuel tank and stores them until they can be released into the air fuel stream for combustion in the engine. The effectiveness of these systems, which typically use activated carbon as the storage medium, is affected by system design, ambient temperature, vehicle use patterns, durability of the system (aging effects), and fuel characteristics including fuel volatility and ethanol content. ⁽¹⁷⁾⁽¹⁸⁾ Optimal pore size characteristics and type of activated carbon, for hydrocarbon fuels, were well defined in the 1980s and investigative work to identify similar information on ethanol was being investigated by 1990. ⁽¹⁸⁾

The EPA regulations for maximum Hot Soak + Diurnal evaporative emissions have become increasingly more stringent. There are two concerns with canister emissions when attempting to meet current and future standards. First are “bleed emissions” for the canister prior to “breakthrough”. Second is the emissions from canister “breakthrough” which is defined by ASTM D 2652 (1999) *Standard Terminology Relating to Activated Carbon* as “the first appearance in the effluent of an adsorbate of interest under specified conditions.” In automotive applications this would be the point where 2.0 grams of hydrocarbon have been emitted from the canister. Breakthrough may be a result of an underdesigned system, or a fuel of high volatility, combined with other factors such as high ambient temperature and certain driving patterns. Bleed emissions during diurnal testing are seldom related to the aforementioned items alone but rather diffusion of hydrocarbons that were already adsorbed in the canister. ⁽¹⁹⁾

In a properly operating system, the canister will store the majority of evaporative hydrocarbon emissions and then the vehicle computer (or mechanical device in older vehicles) will cause them to be released (purged) into the air fuel charge at the appropriate time to combust the vapors.

Ethanol can impact canister operations in two ways. First, numerous studies have shown that higher vapor pressure gasolines generate more evaporative emissions. In the case of conventional gasoline, blends containing ethanol are allowed a higher vapor pressure than other fuels. Secondly, ethanol molecules are not of the same size as hydrocarbon molecules and therefore may not be adsorbed and desorbed at the same rate as hydrocarbons on a specific pore size carbon medium. Vehicles are certified for evaporative emissions on an all hydrocarbon 9.0 psi vapor pressure reference fuel. The effectiveness of the canister on gasoline ethanol blends does not play a role on measurements during the test, but could in real world conditions.

It is entirely possible that the manufacturers of the activated carbon used in the evaporative emissions canisters have addressed this issue. However it has not been possible to verify this through current technical literature.

Recommendation: *Either through a technical literature search or communication with the manufacturers of the activated carbon and canisters it should be determined that the activated carbon and pore size being used are adequate to address proper adsorption and desorption rates of the evaporative emissions from gasoline ethanol blends. If this cannot be verified, research should be undertaken to determine what steps, if any, need to be taken to ensure proper operation of the evaporative emissions control system when operating on gasoline ethanol blends. Since the automakers emission certify their Flexible Fueled Vehicles (FFVs) on E-10, a review of their evaporative control systems approach might be beneficial. Similar activated carbon systems are employed in various vapor control systems throughout the petroleum distribution system (e.g., Stage I and Stage II vapor recovery). Circumstances in this application are similar and any investigation should probably include such stationary applications.*

Section 3 References

1. American Petroleum Institute. 1985. *Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations. API Recommended Practice 1626*. First Edition. April.
2. Renewable Fuels Association. 1999. RFA Publication # 960501 *FUEL ETHANOL Industry Guidelines, Specifications, and Procedures*. October.
3. Renewable Fuels Association. 1998. *Gasoline Ethanol Blends-Programs Operations Guide*. RFA Recommended Practice# 930601. September.
4. Downstream Alternatives Inc. 1996. *Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide*. January.
5. American Society for Testing and Materials (ASTM). 2001. *Standard Specification for Automotive Spark-Ignition Engine Fuel*. Designation D 4814-01. July.
6. Bechtold, Richard L. 1997. *Alternative Fuels Guidebook*. April.
7. Federal Register. 1979. *Gasohol Waiver*. Vol. 44, No. 681. April.
8. Oak Ridge National Laboratory. 2002. Correspondence from Jerry Hadder on "CRC Handbook Chemistry & Physics." February 11.
9. Owen, Keith and Trevor Coley. 1990. *Automotive Handbook*.
10. D'Ornellas, C.V. 2001. *The Effect of Ethanol on Gasoline Oxidation Stability*. SAE Paper # 2001-01-3582. September.
11. California Air Resources Board (CARB). 1996. *CaRFG Performance and Compatibility Test Program*. March.
12. Downstream Alternatives Inc., Robert E. Reynolds. 2000. *Fuel Permeation of Automotive Fuel System Elastomers and Permeation Issues Related to Ethanol, MTBE, and Aromatics*. Prepared for the Renewable Fuels Association. February 23.
13. U.S. Environmental Protection Agency (EPA). 1999. *Control of Air Pollution from New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements*. 40 CFR Parts 80, 85, and 86 [AMS-FRL-] RIN (2060-A123).
14. Coordinating Research Council (CRC). 2002. *Fuel Permeation from Automotive Fuel Systems*. Work Plan for CRC Project No. E-65-1. October 14.

15. Stevens, R.D. 2001. *Permeation and Stress Relaxation Resistance of Elastomeric Fuel Seal Material*. SAE Paper # 2001-01-1127. March 5.
16. Stevens, R.D. 2002. *A New Fluoroelastomer for Fuel System Seals*. Ronald D. Stevens. SAE Paper # 2002-01-0632 . March 4.
17. Urbanic, J.E. *et.al.* 1989. *Factors Affecting the Design and Breakthrough Performance of Evaporative Loss Control Systems for Current and Future Emission Standards*. SAE Paper # 890621. February 27.
18. Johnson, H.R. and R.S. Williams. 1990. *Performance of Activated Carbon in Evaporative Loss Control Systems*. SAE Paper # 902119. October 22.
19. Williams, Roger S. and C. Reid Clontz. 2001. *Impact and Control of Canister Bleed Emissions*. SAE Paper # 2001-01-0733. March 5.

Section 4

**Fuel Volatility - Vapor Pressure, Distillation Properties,
Vapor Lock Protection Class, and Driveability Index**

4.0 Fuel Volatility - Vapor Pressure, Distillation Properties, Vapor Lock Protection Class, and Driveability Index

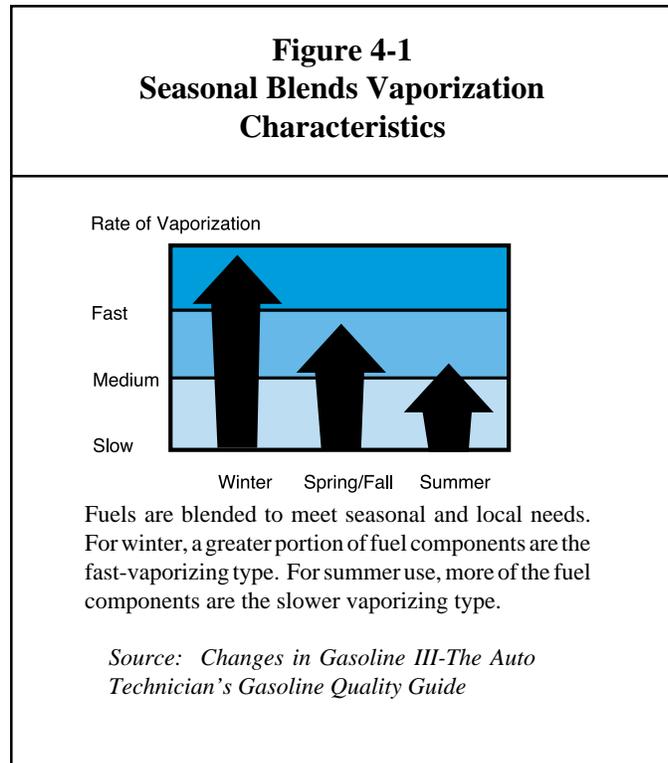
Two primary references (1, 2) were relied on heavily for many portions of this section. Gasoline is metered in liquid form, through the fuel injectors (or carburetor), and mixed with air and atomized before entering the cylinders. It is very important that a fuel's tendency to evaporate is controlled to certain standards. A fuel's ability to vaporize, or change from liquid to vapor, is referred to as its volatility and is an extremely important characteristic of gasoline. Fuel volatility can effect several areas of vehicle performance as listed in Table 4-1.

Table 4-1 Effects of Gasoline Volatility on Vehicle Performance	
<u>Volatility Too Low</u>	<u>Volatility Too High</u>
Poor cold start	High evaporative emissions/ Canister overload & purge
Poor warm up performance	Hot driveability problems/ vapor lock
Poor cool weather driveability	Fuel economy may deteriorate
Increased deposits -crankcase -combustion chamber -spark plugs	
Unequal fuel distribution in carbureted vehicles	
<i>Source: Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide</i>	

Gasoline which is not volatile enough results in poor cold start and poor warm up driveability. These fuels can also contribute to crankcase and combustion chamber deposits as well as spark plug deposits.

Gasoline which is too volatile, vaporizes too easily and may boil in fuel pumps, fuel lines or in carburetors, at high operating temperatures. If too much vapor is formed, this could cause a decrease in fuel flow to the engine, resulting in symptoms of vapor lock, including loss of power, rough engine operation, or complete stoppage. Fuel economy could also deteriorate and evaporative emissions could increase.

In order to assure that fuels possess the proper volatility characteristics, refiners adjust gasoline seasonally, providing more volatile gasoline in the winter to provide good cold start and warm up performance. In the summer, gasoline is made less volatile to minimize the incidence of vapor lock and hot driveability problems and to comply with



environmental standards. Adjustments are also made for geographic areas with high altitudes. This is done because it requires less heat for a liquid to boil at higher altitudes.

There are four key parameters to measure fuel volatility, vapor pressure, distillation curve, vapor lock protection class, and driveability index. ASTM provides standards and test procedures for each of these parameters which are discussed in more detail below.

4.1 Vapor Pressure

The vapor pressure of a fuel must be high enough to provide ease of starting the engine but not so high as to contribute to vapor lock or excessive evaporative emissions. The Vapor Pressure measurement can be performed by a variety of laboratory procedures and automated measurement devices. One test procedure, referred to as the “Reid Method” is performed by submerging a gasoline sample (sealed in a metal sample chamber) in a 100° F water bath. More volatile fuels will vaporize more readily, thus creating more pressure on the measurement device and higher readings. Less volatile fuels will create less vapor and therefore give lower readings. The vapor pressure measurement from the Reid test method is referred to as Reid Vapor Pressure or RVP. Because of the earlier popularity of this test method, the term RVP has become a widely used term when referring to vapor pressure. However, the “Reid” in Reid Vapor Pressure merely designates the method used to determine the vapor pressure or VP at 100° F. As other test procedures have become more popular, the term vapor pressure or VP is becoming more common, although the term RVP is still frequently used because it is more clearly understood to be the vapor pressure at a specific test temperature. In subsequent references to the term “vapor pressure “ or “VP” in this paper, the reader should understand that the vapor pressure test temperature is 100° F.

The vapor pressure of ethanol is only 2.3 psi⁽³⁾ However, when ethanol is added to gasoline at low levels, a non-ideal mixture is formed resulting in a fuel with a higher vapor pressure than either liquid by itself. For example, a gasoline with a 10.0 psi vapor pressure, when blended with ethanol at the 2 v% to 10 v% range, would typically increase to the 10.5 to 11.0 psi vapor pressure range. The exact increase is dependent upon the vapor pressure and composition of the base fuel. Lower aromatic fuels tend to exhibit a slightly greater vapor pressure increase. As a guideline, denatured ethanol is generally assumed to have a blending vapor pressure (BVP) of 17.0 psi.⁽⁴⁾

The following table provides an example of calculating the estimated vapor pressure resulting from adding 10 v% ethanol to a base gasoline with a vapor pressure of 8.0 psi.

Table 4-2 Estimated Vapor Pressure of Gasoline Ethanol Blend from Adding 10 v% Ethanol		
	<u>Blending Vapor Pressure (BVP)</u>	<u>Contribution to Finished Vapor Pressure</u>
Gasoline	8.0	7.2
Ethanol	17.0	1.7
Estimated Vapor Pressure of gasoline ethanol blend	n/a	8.9

In the above example, the vapor pressure of the gasoline ethanol blend is 0.9 psi higher than the base gasoline. This increase in vapor pressure experienced in low level ethanol blends can be important if the refiner must adjust the base fuel to accommodate the vapor pressure increase resulting from the addition of ethanol. For instance, finished summer grade RFG must be of very low vapor pressure in order to comply with the evaporative emissions component of the U.S. Environmental Protection Agency (EPA) Complex Model. A fuel with a targeted vapor pressure of 7.2 psi would need to be near, or in some cases slightly below, 6.0 psi to accommodate the addition of ethanol. Consequently, refiners would need to remove butane and/or pentane to properly formulate the base fuel. The cost of rejecting such components must be considered by the refiner.

The EPA currently allows summer grade CG containing 9 v% to 10 v% ethanol to be of 1.0 psi higher vapor pressure than other CG and applies no vapor pressure restrictions on winter grades. Some states, often with ozone compliance problems, do not allow such exemptions for gasoline ethanol blends. In the latter case, refiners would need to make economic comparisons similar to those considered for summer grade RFG.

The economics of rejecting butane and pentane, to accommodate ethanol blending in areas without an RVP allowance, must be considered by the refiner and generally results in an economic penalty against ethanol's value as a blending component. Of course in a refinery setting the calculations of any such penalty are more complex. The refiner would include ethanol in its linear program model as an available component and any economic benefit or penalty would be calculated considering all other factors such as the available crude slate, other merchant components available, the finished product slate, and the value of any refinery stream rejected to other uses.

Ethanol's higher blending vapor pressure is a major drawback from a refiner's perspective.

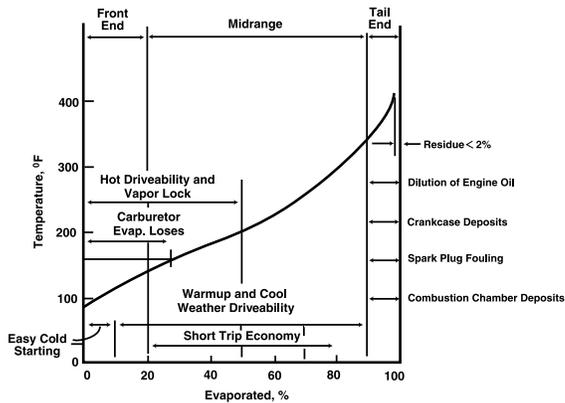
Over the years there have been various attempts to identify additives to reduce or eliminate the vapor pressure increase resulting from ethanol addition. None have resulted in identifying any additive that would be effective at low concentration levels (i.e., below 1 v% of the total blend).

Recommendation: *Given that no other researchers have found an effective vapor pressure reducing additive it is unlikely that additional research would be successful. However, it might be worthwhile to at least survey some researchers to determine if they believe some other approach to researching this issue could prove fruitful.*

4.2 Distillation Properties

The distillation test is used to determine fuel volatility across the entire boiling range of gasoline. Gasoline consists of a variety of chemical components that evaporate at different temperatures. More volatile components (faster vaporizing) evaporate at lower temperatures, less volatile (slower vaporizing) ones at higher temperatures. The plotting of these evaporation temperatures is referred to as a distillation curve (see figure 4-2). The ASTM

**Figure 4-2
Importance of Proper Distillation**



Gasoline significantly below the curve (increased volatility) would provide easier starting, better warm-up and be less likely to contribute to deposits but would have higher evaporative losses and be more likely to contribute to vapor lock.

Gasoline significantly above the curve (decreased volatility) would have fewer evaporative losses and be less likely to vapor lock. Also, short trip economy would improve. However, ease of starting and warm up would suffer and deposits and dilution of engine oil could increase. Exhaust emissions may also increase in some cases.

Source: Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide

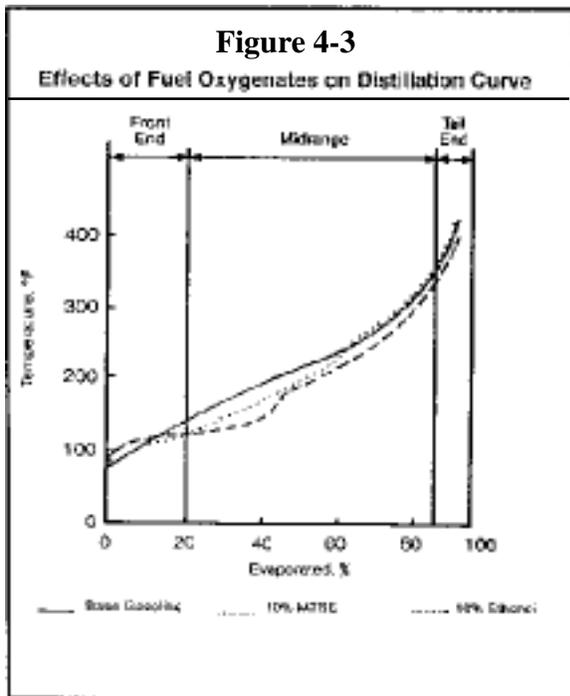
specifications set temperature ranges at which 10%, 50%, and 90% of the fuel will be evaporated as well as at what temperature all the fuel has evaporated (referred to as end point). Each point affects different areas of vehicle performance.

The 10% evaporated temperature (T_{10}) must be low enough to provide easy cold starting but high enough to minimize vapor lock/hot driveability problems. The 50% evaporated temperature (T_{50}) must be low enough to provide good warm up and cool weather driveability without being so low as to contribute to hot driveability and vapor locking problems. This portion of the gallon also affects short trip economy. The 90% evaporated temperature (T_{90}) and end point (EP) evaporation temperature

must be low enough to minimize crankcase and combustion chamber deposits as well as spark plug fouling and dilution of engine oil.

Distillation characteristics may vary based on the availability of gasoline components. This should not alter performance characteristics of the gasoline unless the alteration is severe. Depending on the distillation class, 10% of the fuel would be evaporated prior to reaching a temperature of 122°F to 158°F, 50% prior to reaching a temperature of 150°F to 250°F and ninety percent prior to reaching a temperature of 365°F to 374°F. All of the fuel should be evaporated by 437°F. The ranges between these temperatures provide for adjustment in volatility classes to meet seasonal changes.

When ethanol is added to gasoline it alters the distillation curve, especially the T_{50} . The T_{50} may be lowered by 20°F or more. This is illustrated in Figure 4-3.



If the base gasoline has a low T₅₀, the addition of ethanol could drop the T₅₀ below the ASTM specifications. This, in turn, could result in poorer hot weather driveability and increase evaporative emission losses. The T₅₀ of gasoline is also a major factor in calculating driveability index, which is covered later in this report section.

4.3 Vapor Lock Protection Class

ASTM also specifies a vapor lock protection class to minimize the incidence of vapor lock due to gasoline volatility. Similar to vapor pressure and distillation temperatures, the vapor lock protection class varies depending on climate and altitude. There are six vapor lock protection classes numbered 1 through 6. The requirement for each class is the test temperature required to create a maximum vapor to liquid ratio of 20 using ASTM test method *D 2533 Standard Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels* or *D 5188 Standard Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)*. This measurement is commonly referred to as TV/L20. Summer grades require higher TV/L20 temperatures while more volatile winter grades can have lower TV/L20 temperatures. For instance, vapor lock protection Class 1 would have a TV/L20 of 140°F (60°C) while the more volatile Class 6 would have a TV/L20 maximum of 95°F (35°C). In other words it would take less heat for Class 6 gasoline to create the same amount of vapor created by much more heat in Class 1.

The Vapor Lock Protection Class requirements are listed in the following table.

Table 4-3 Vapor Lock Protection Class Requirements		
Vapor Lock Protection Class	Vapor/Liquid (V/L) ^{AB}	
	Test Temperature °C (°F)	V/L, max
1	60 (140)	20
2	56 (133)	20
3	51 (124)	20
4	47 (116)	20
5	41 (105)	20
6	35 (95)	20

A At 101.3 kPa pressure (760 mm Hg.)
 B The mercury confining fluid procedure of test Method D 2533 shall be used for gasoline-oxygenate blends. Test Method D 5188 may be used for all fuels. The procedure for estimating temperature-V/L may only be used for gasoline.

Source: ASTM D 4814

Since ethanol has a lower boiling point than many of the components in gasoline, it tends to lower the temperature at which a maximum V/L ratio of 20 is reached (i.e., more vapor formed from less heat). The temperature of the fuel system and the V/L it can tolerate without symptoms of vapor lock vary from vehicle to vehicle and with ambient conditions and operating conditions. However, TV/L20 has proven reasonably accurate at predicting the tendency of a fuel to cause vapor lock. A similar relationship for gasoline oxygenate blends has also been determined.⁽⁵⁾

The Coordinating Research Council (CRC) continues to research the predictive accuracy of TV/L20 for both gasoline and gasoline ethanol blends as well as alternative formulas that may prove more accurate.^(6, 7, 8)

4.4 Driveability Index

The ASTM specification also includes a recently added Driveability Index. Based on data compiled by CRC and others, the ASTM Driveability Task Force, long ago, determined that there is a relationship between fuel distillation properties and vehicle driveability. While control of T₁₀, T₅₀, T₉₀, and end points have traditionally been used to help address this relationship for cold start or warm up performance, the relationship can be expressed by a Driveability Demerit Model that can estimate vehicle driveability demerits during cold start and warm up. The predictive model is a function of ambient temperature and fuel volatility expressed by certain distillation temperatures at which the fuel evaporates. The Driveability Index (DI) is a simplification of the model that can be more easily applied. The DI formula is expressed as:

$$DI = (1.5 \times T_{10}) + (3.0 \times T_{50}) + (1.0 \times T_{90})$$

A detailed explanation of how the DI equation was developed can be found in SAE Paper # 881669 (9).

As an example, assume that a Class C conventional gasoline has a T₁₀ of 130°F, a T₅₀ of 200°F, and a T₉₀ of 360°F, the formula would be applied as :

$$DI = (1.5 \times 130) + (3.0 \times 200) + (1.0 \times 360) = 1155$$

(the formula can also be expressed as degrees centigrade)

The DI of the fuel in the above example is 1155. Generally speaking, fuels with DIs above the 1200 - 1250 range exhibit poorer cold start and warm up performance than fuels below that range. The ASTM standards set a range of DI maximum from 1250 in summer grade down to 1200 for winter grade (when cold start and warm up performance is more critical).

As with other ASTM standards, this formula continues to be reviewed for its accuracy as a predictive tool. One issue is that the DI was originally developed in older technology vehicles. Of

more concern, it was developed on hydrocarbon only fuels. Consequently it is not as accurate at predicting the cold start and warm up performance of oxygenated fuels, especially gasoline containing ethanol. Because of this, the auto manufacturers have suggested an oxygen adjustment factor^(10, 11) of 20 points per wt% oxygen on the Fahrenheit scale (11 points on the centigrade scale) resulting in the following formula:

$$DI = (1.5 \times T_{10}) + (3.0 \times T_{50}) + (1.0 \times T_{90}) + (20 \times \text{wt\% O}_2)$$

It is thought that this adjustment is needed because of the oxygen content of the fuel, and in the case of ethanol, possibly because of ethanol's higher heat of vaporization. The heat of vaporization of hydrocarbons vary but not significantly, while the heat of vaporization of polar molecules is quite different from non-polar. This means that as the content of ethanol in gasoline changes, the effect of temperature on pressure changes as well.⁽⁸⁾ The DI formula, as included in current ASTM specifications does not reflect this.

Using the example of the 1155 DI gasoline calculated above, and assuming the addition of 10V% ethanol would reduce the T_{50} by 20°F, using the new T_{50} and applying the oxygen adjustment factor would result in the following.

$$DI = (1.5 \times 130) + (3.0 \times 180) + (1.0 \times 360) + (3.5 \times 20) = 1165$$

So comparing the hydrocarbon to ethanol blend, the DIs are nearly the same with the oxygen correction factor whereas without it the DI of the ethanol blend would be 70 points lower or 1095 compared to 1155 for the all hydrocarbon fuel. Where the oxygen correction factor could become of concern is in fuels that are already at the edge of DI compliance and where ethanol might have a greater impact on T_{50} . An example comparing a Volatility Class AA hydrocarbon fuel to an ethanol blend could be as follows:

$$\begin{array}{l} \text{Hydrocarbon Fuel} \quad T_{10} = 140 \quad T_{50} = 220 \quad T_{90} = 370 \\ (1.5 \times 140) + (3 \times 220) + (1.0 \times 370) = \text{DI } 1240 \end{array}$$

$$\begin{array}{l} \text{Ethanol Blend} \quad T_{10} = 140 \quad T_{50} = 205 \quad T_{90} = 370 \\ (1.5 \times 140) + (3 \times 205) + (1.0 \times 370) = (3.5 \times 20) = \text{DI } 1265 \end{array}$$

In the above comparison, the hydrocarbon fuel would be under the specified DI of 1250 for Volatility Class AA while the ethanol blend, after utilizing the oxygen correction factor, would be over the specified DI of 1250. Consequently, if too high an oxygen adjustment factor is adopted, it could be detrimental to ethanol use.

Currently the DI is enforced at the refinery gate, although the automakers and some regulatory entities would prefer it be enforced at retail or, at least, the terminal level. However, this is problematic because of commingling fuels in the system. Mixing two fuels with complying DIs could result in a fuel with a non-compliant DI.

A second problem is that jobbers and retailers typically blend their ethanol into gasoline at the terminal. They do not possess the necessary equipment to calculate the DI and obviously could not leave the load on the truck while waiting days for test results from an independent lab. So moving enforcement to the retail level could cause enough concern about compliance or unintentional violations to discourage some companies from blending ethanol.

It is also important to note the auto manufacturer's and petroleum industry's position on this issue. The automakers are concerned about high DI levels because the low volatility fuels used to comply with today's lower fuel volatility requirements, in both RFG and conventional gasoline, tend to result in gasolines with higher DIs. One concern is that this could lead to greater driveability complaints. And, in fact, some auto manufacturers have issued Technical Service Bulletins, about high DI fuels, to their dealership service networks.⁽¹²⁾ The proliferation of lower volatility fuels have led to the automakers supporting a maximum DI of 1200 for all fuels.^(10, 11)

A second implication is that the automakers also use the DI formula calling it "Distillation Index" (also DI) using the identified formula but using it as a predictive tool for emissions. They

maintain that fuels of too high Distillation Index (i.e., above 1200) increase exhaust emissions of hydrocarbons and toxics and have in fact, in the past, petitioned the U.S. EPA to adopt federal standards implementing a DI maximum of 1200 and including an oxygen content offset ⁽¹⁰⁾. The automakers have also argued that lower DI levels would allow them to calibrate engine control systems within a narrower range thereby resulting in additional emissions reductions in future technology vehicles.

The petroleum industry opposes more stringent DI standards because it could put further restraints on refining operations, limiting the use of certain components. The NPC ⁽¹³⁾ found based on refinery LP modeling, that a 50°F reduction in the refinery gate DI from 1250°F to 1200°F would require an investment as much as \$11 billion and could increase the cost of gasoline by 7.0 cents per gallon. The auto manufacturers also commissioned a study on this topic ⁽¹⁴⁾ which put estimates for investment requirements at only \$140 million and a national average increase in gasoline cost of only 0.4 cents per gallon. The refining industry has also generally opposed moving the compliance point downstream of the refinery gate. To do so would require them to make even lower DI fuels to allow for a larger compliance margin due to commingling fuels in terminals, ships, etc.

These issues will, of course, continue to be studied and debated. However, it will be important that any changes adopted, which may incorporate an oxygen offset, not be so restrictive as to reduce ethanol use.

It is important to note that ASTM D 4814 defines specifications on Vapor Pressure/Distillation Class gasoline for each state (or in some cases, portions of a state) by month. These requirements also specify the vapor lock protection class. Consequently, the entire specification should be consulted to determine the appropriate fuel properties for the area and time frame in which the gasoline will be sold

The following table recaps the standards for vapor pressure, distillation temperatures and DI for each of the vapor pressure/distillation classes of gasoline.

Table 4-4 ASTM D 4814 GASOLINE VOLATILITY REQUIREMENTS

Vapor Pressure Dist. Class	Distillation Temperatures				Vapor Pressure psi/Max. (kPa) @ 100°F	Driveability Index max F° (C°) Derived
	10% Evap. Max. F° (C°)	50% Evap. Min.-Max. F° (C°)	90% Evap. Max. F° (C°)	End Point Max. F° (C°)		
AA	158 (70)	170-250 (77-121)	374 (190)	437 (225)	7.8 (54)	1250 (597)
A	158 (70)	170-250 (77-121)	374 (190)	437 (225)	9 (62)	1250 (597)
B	149 (65)	170-245 (77-118)	374 (190)	437 (225)	10 (69)	1240 (591)
C	140 (60)	170-240 (77-116)	365 (185)	437 (225)	11.5 (79)	1230 (586)
D	131 (55)	150-235 (66-113)	365 (185)	437 (225)	13.5 (93)	1220 (580)
E	122 (50)	150-230 (66-110)	365 (185)	437 (225)	15 (103)	1200 (569)

Section 4 References

1. Downstream Alternatives Inc. 1996. *Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide*. January.
2. American Society for Testing and Materials (ASTM). 2001. *Standard Specification for Automotive Spark-Ignition Engine Fuel*. Designation D 4814-01. July.
3. Bechtold, Richard L. 1997. *Alternative Fuels Guidebook-Properties, Storage, Dispensing, and Vehicle Facility Modifications*. Society of Automotive Engineers. April.
4. Piel, William J. 1991. *Use of MTBE and Other Oxygenates in Oxygenated Gasolines*. Presented at SAE Fuels TopTec. August 28-29.
5. American Society for Testing and Materials (ASTM). 2001. *Standard Specification for Automotive Spark-Ignition Engine Fuel. Appendix XI.10 Vapor-Liquid Ratio*. Designation D 4814-01. July.
6. Coordinating Research Council (CRC). 2000. *1999 CRC Hot-Fuel-Handling Program*. CRC Report No. 623. August.
7. Coordinating Research Council (CRC). 2001. *2000 CRC Intermediate-Temperature Volatility Program*. CRC Report No. 626. June.
8. Coordinating Research Council (CRC). 2002. *2001 CRC Hot-Fuel-Handling Program*. CRC Report No. 629. June.
9. Barke, D.A. et.al. _____. *The Development and Proposed Implementation of the ASTM Driveability Index for Motor Gasoline*. SAE Paper #881668. October 10.
10. *Petition to Regulate Gasoline Distillation Properties*. 1999. Submitted to U.S. EPA by DaimlerChrysler Corporation, Ford Motor Company, General Motors Corporation, and The Association of International Automobile Manufacturers. January 26.
11. Ford Motor Company. 1996. *Ford Position on the Effects of Fuel Quality on Vehicle Performance and Emissions - Edition 10. (Ford Position on the Effects of Fuel Volatility and the Recommended Driveability Index)*.
12. Chrysler Corporation. 1997. Technical Service Bulletin No. 14-08-97 . *Subject: Poor Driveability With High DI (Driveability Index) Fuel*. November 21.
13. National Petroleum Council. 2000. *U.S. Petroleum Refining-Assuring the Adequacy and Affordability of Cleaner Fuels*. June.

14. MathPro. 1998. *Final Report - Technical and Economic Implications of Controlling the Distillation Index of Gasoline*. Prepared for American Automobile Manufacturers Association under AAMA Agreement No. MP9813-823. October.

Section 5
World-Wide Fuel Charter

5.0 World-Wide Fuel Charter

While ASTM D 4814 *Standard Specification for Automotive Spark-Ignition Engine Fuel* is the industry accepted standard for spark-ignition engine fuels, the auto manufacturers do not feel ASTM has addressed all of the issues about which they are concerned. As a result they[†] have developed their own fuel quality document called the “World-Wide Fuel Charter”.⁽¹⁾

ASTM specifications are established by consensus, based on the broad experience and close cooperation of producers of transportation fuels, manufacturers of automotive equipment, and users of both types of products. Gasoline must cover a wide range of operating conditions, such as variations in fuel systems, engine temperatures, a variety of climates, altitudes, and driving patterns. The general industry view is that the properties of gasoline must be balanced to give satisfactory engine performance over an extremely wide range of circumstances. Consequently, prevailing ASTM standards represent compromises so that the numerous performance requirements may be satisfied, thereby making it possible to satisfy the requirements of hundreds of millions of spark-ignition engines with just a few grades of gasoline.⁽²⁾

Conversely, the WWFC represents what the auto manufacturers consider to be more ideal fuels, based on their concerns. Additionally, the requirements in the WWFC are designed not just for performance but to aid the auto manufacturer in meeting the ever tightening emissions requirements with which they must comply. Finally, the globalization of the auto industry has led to an overall effort for worldwide fuel standards harmonization. Such fuel standards harmonization would allow more widespread use of certain automobile emissions control strategies in a larger number of countries.

The WWFC includes provisions for both gasoline and diesel fuel and includes technical background sections on each. Here we are only concerned with gasoline in general and the treatment of ethanol in particular.

In the case of gasoline, the charter includes four categories as follows:

[†] European Automobile Manufacturers Association (ACEA), Alliance of Automobile Manufacturers (AAM), Engine Manufacturers Association (EMA), Japan Automobile Manufacturers Association (JAMA), and associate members: Association Mexicana de la Industria Automotriz, A.C. (AMIA), Canadian Vehicle Manufacturers' Association (CVMA), Chamber of Automotive Manufacturers of the Philippines, Inc. (CAMPI), Chinese Association of Automotive Industry, Korean Automobile Manufacturers Association (KAMA), National Association of Automobile Manufacturers of South Africa (NAAMSA), Thai Automotive Industry Association (TAIA)

Category 1: Markets with no or minimal requirements for emission control; based primarily on fundamental vehicle/engine performance concerns.

Category 2: Markets with stringent requirements for emission control or other market demands. For example, markets requiring US Tier 0 or Tier 1, EURO 1 and 2, or equivalent emission standards.

Category 3: Markets with advanced requirements for emission control or other market demands. For example, markets requiring US California LEV, ULEV and EURO 3 and 4, or equivalent emission standards.

Category 4: Markets with further advanced requirements for emission control, to enable sophisticated NO_x and particulate matter after-treatment technologies. For example, markets requiring US California LEV-II, US EPA Tier 2, EURO 4 in conjunction with increased fuel efficiency constraints or equivalent emission standards. These fuel quality recommendations are for the properties of the finished fuel as provided to the end user. Internal quality control methods are not dictated or restricted, as long as the fuel meets these specifications. Where national requirements are more severe than these recommendations, those national limits have to be met. To meet future customer, environmental and energy challenges, the automotive industry is exploring advanced propulsion technologies worldwide. While Category 3 has been defined as those requirements needed by advanced technologies, as they exist today, Category 4 has been defined as a sulfur-free fuel to meet the needs of future vehicle technologies. Other parameters in Category 4 are expected to be revised in future editions, as the needs of future vehicle technologies become better known. All the Categories will be reviewed and revised as appropriate to reflect changes in vehicle technologies and/or petroleum refining.

In all categories, oxygen content is limited to a maximum of 2.7 wt% but footnoted as follows:

“Where oxygenates are used, ethers are preferred. Where up to 10% of volume ethanol (meeting ASTM D 4806 and a pH of 7 - 9) is permitted by preexisting regulations, the blended fuel must meet all other Category x requirements. Higher (C > 2) alcohols are limited to 0.1 % maximum by volume. Methanol is not permitted.”

Obviously having the world’s auto manufacturers state that ethers are preferred over ethanol is not an ideal situation for expanded use of ethanol in gasoline.

In the “Technical Background for Harmonized Fuel Recommendations” section, the WWFC makes further negative statements about oxygenates in general and ethanol in particular. The following is excerpted from the report:

“OXYGENATES

Oxygenated organic compounds, such as MTBE and ethanol, are often added to gasoline to increase octane, to extend gasoline supplies, or to induce a lean shift in engine stoichiometry to reduce carbon monoxide emissions. The leaner operation reduces carbon monoxide emissions, especially with carbureted vehicles without electronic feedback controlled fuel systems.

These emission benefits are not realized as much in modern electronic feedback controlled vehicles because the leaning effect only occurs during cold operation or during rapid accelerations. In fact, fuel leaning caused by oxygenates can degrade driveability depending on the leanness of the engine’s base calibration with all-HC (ie., non-oxygenated) gasoline. This over-leaning can also cause emissions to increase. Because ethanol has a higher heat of vaporization than ethers, some of the driveability degradation of gasoline oxygenated with ethanol can be attributed to the additional heat needed to vaporise the gasoline.

The California Air Resources Board (CARB) conducted emission tests on 14 1990-1995 vehicles using 2 gasolines with 10% ethanol and 11% MTBE. When the ethanol fuel was compared to the MTBE fuel, it decreased toxic emissions by 2% and CO by 10%, but it increased NOx by 14%, total HC by 10% and Ozone Forming Potential by 9%.

Based on past experience with impurities in ethanol that have led to degradation of fuel systems, fuel ethanol must have a specification to control pH and its blending properties (ASTM D 4806). The limits and restriction on the oxygenates permitted in each Category were developed on the basis of emission benefits, vehicle performance and pre-existing regulations. Thus, when oxygenates are used, ethers are preferred.

Methanol is not permitted. Methanol is an aggressive material which can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers.

Importantly, some auto manufacturers have started advising owners of their recent model year autos that they recommend the use of gasoline that meets the WWFC specifications if they are available. †

Other sections of the WWFC include additional provisions that could impact ethanol use, including an oxygen offset in the DI equation (see section 4.4). The specification requires an 11 point adjustment (on the centigrade scale) for each weight percent of oxygen which equates to 20 points on the Fahrenheit scale.

The WWFC also includes more stringent T_{50} standards on winter grade gasolines than does the ASTM Standards. The WWFC requires that minimum T_{50} not be below 77° C (170°F) on all gasoline while ASTM specifications for the Class D and E winter grades permit a minimum T_{50} of 66°C (150°F). The automakers outspokenly opposed lowering the T_{50} minimum in ASTM D4814 at the time it was done.

The charter also includes more stringent specifications on other fuel characteristics unrelated to oxygenates or ethanol such as sulfur content, silicon contamination, and the use of methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline.

It is important to note that the World-Wide Fuel Charter specifications were designed solely from an auto manufacturer perspective, considering their needs to meet various regulatory requirements (e.g., emissions controls) as well as minimizing any incidence of consumer complaints resulting from driveability problems that could be caused, in part, by fuels.

These recommendations do not, of course, consider the many public policy considerations involved in the use of alternative fuels such as reduction of imported transportation energy fuels and/or crude oil, and use of domestic renewable resources.

† Vehicle owners manuals, Model Year 2003 Fuel recommendations-Daimler Chrysler, Ford, GM, Isuzu, Saab, Toyota/Lexus

While the WWFC is not a fuels regulation, the automakers have established a program to identify gasoline companies offering fuels that meet the WWFC specifications. To date, no U.S. petroleum company has attempted to be so identified. In Canada, the auto manufacturers have implemented the “Automakers Choice” fuel endorsement program. A specifically designed “happy pump, happy car”, Automakers Choice logo identifies pumps which sell gasoline meeting auto manufacturers specifications.

Recommendations: *The various U.S. government agencies, as well as their counterparts in other countries, need to initiate a dialogue with the auto manufacturers concerning the World-Wide Fuel Charter and global fuels harmonization initiatives. The auto manufacturers need to be made acutely aware of various policies and initiatives that would result in changes to existing and future transportation fuels. When the WWFC is in contrast with public policy objectives, those issues need to be thoroughly discussed to determine if more suitable specifications and text can be utilized in the WWFC. Similarly, this will give the automakers an avenue to explain, in detail, why certain aspects of the WWFC seem to contradict some energy related public policy objectives.*

Note: The World Wide Fuel Charter (April 2000) is currently being updated. The auto manufacturers organizations are considering an updated version that is currently in “Draft for Comments” status. The draft contains additional text on oxygenates and a brief section on E diesel™. Both the current WWFC and the draft can be obtained via the Internet at www.autoalliance.org.

Section 5 References

1. European Automobile Manufacturers Association (ACEA), Alliance of Automobile Manufacturers (AAM), Engine Manufacturers Association (EMA), Japan Automobile Manufacturers Association (JAMA). 2000. *World-Wide Fuel Charter*. April.
2. Downstream Alternatives Inc. 1996. *Changes in Gasoline III-The Auto Technician's Gasoline Quality Guide*. January.

Section 6
Regulating Entities

6.0 Regulating Entities

There are a number of regulating entities involved in regulating the characteristics of transportation fuels. These include organizations concerned with fuel quality, environmental impact, consumer protection, etc. These entities include nearly every level of government, but especially at the federal and state levels. The actions, or in some cases, inactions, of these entities could impact the marketability and value of ethanol as a gasoline component.

6.1 Federal Regulatory Agencies and Departments

There are various federal agencies and departments with varying degrees of regulatory oversight of, or involvement with, transportation fuels.

6.1.1 U.S Environmental Protection Agency (EPA)

At the top of the federal list is the U.S. Environmental Protection Agency (EPA). The EPA regulates both conventional and reformulated gasoline. Some examples of EPA fuel related actions that have impacted ethanol use include the following:

Lead Phasedown: Lead phasedown/phaseout was largely positive for ethanol since removal of lead from the gasoline pool resulted in greater use of ethanol for its octane value.

Phase I and Phase II Volatility Controls: Phase I and Phase II Volatility Controls required reductions in gasoline vapor pressure during summer months. However, EPA granted gasoline ethanol blends containing 9-10 v% ethanol a waiver of up to 1.0 psi above the specified standard for conventional gasoline. Had the agency not done so, ethanol use would not only have stopped increasing, but most likely would have declined.

Oxygenated Fuel Programs: Oxygenated fuel programs in CO non-attainment areas are technically state programs, but they were required by federal legislation and the regulations implementing them

were written by EPA. Oxygenated fuel programs were, of course, a positive development for expanded ethanol use.

Reformulated Gasoline (RFG): Here again, the regulations implementing the legislation requiring RFG were written by EPA, as were numerous related guidance documents. In this instance, a volatility exemption, in the form of a 1.0 psi vapor pressure waiver, was not granted to RFG containing ethanol. This has, in part, contributed to the limited use of ethanol in RFG. In addition, EPA developed the “Complex Model” used in both Phase I and Phase II of the RFG program. The input into these mathematical equations was based largely on actual emissions test results from large peer reviewed research programs such as the Auto/Oil Air Quality Improvement Research Program (AQIRP) and similar test programs. The values assigned to such items as oxygen content, vapor pressure, and distillation properties in these models affect the operational practicality and refinery economics of using ethanol since ethanol impacts all of these properties.

Anti-dumping Regulations: The EPA also developed and implemented regulations to comply with the anti-dumping provisions of the 1990 Clean Air Act Amendments. This program was implemented to prevent gasoline components, that contribute to emissions, being removed from RFG and simply moved into the conventional gasoline (CG) pool. How ethanol is treated in these baselines and compliance calculations has generally been favorable towards the use of ethanol in CG.

Mobile Source Air Toxics (MSAT) Rule: Under MSAT requirements for CG and RFG, refiners must maintain their average 1998-2000 toxics performance levels, which were better than what regulations required, for benzene, formaldehyde, acetaldehyde, 1,3-butadiene, and polycyclic organic matter, identified as toxic air pollutants. All five of these air toxics are known or probable human carcinogens. Levels of air toxics from mobile sources are decreasing as a result of EPA’s clean air programs that have produced cleaner cars and cleaner burning gasoline. For example, benzene levels

in urban areas have decreased nationwide by almost 40 percent between 1993 and 1998. This trend is expected to continue because of more stringent standards for cars and light- and heavy-duty trucks and cleaner diesel fuel. The MSAT rule, which went into effect in 2002, helps to ensure that the positive steps already taken to reduce MSATs will continue. Because motor vehicles emit a variety of toxic air pollutants, EPA will begin in 2003 to re-evaluate emissions of these pollutants to ensure adequate protection of public health and the environment.⁽⁴⁾

Tier II Fuel Regulations: The EPA included provisions in their Tier II regulations that require manufacturers to use ethanol blended fuels when aging their fuel system components (e.g., elastomers and composites) for compliance testing. This will result in manufacturers considering gasoline ethanol content when developing fuel system components. This will ensure the materials compatibility of automotive fuel system components with ethanol blends in the future.

The point of the above examples is that, perhaps more than any other agency, the actions EPA takes regulating transportation fuels can affect the marketability of ethanol.

6.1.2 U.S. Department of Energy (DOE)

The U.S. Department of Energy (DOE) can also play a role in developing regulations to implement various legislation and is often charged with examining the feasibility of various programs for timing and implementation. For instance, provisions pertaining to clean fuels programs often call for the EPA administrator to consult with the Secretary of Energy on supply availability and similar issues. Additionally, members of Congress often call upon DOE to study various issues being considered for legislation. The DOE is also charged with monitoring the progress of complying with the Energy Policy Act (EPACT). Consequently, although their regulatory activities may not be as extensive as EPA's, the Department's actions can still play a significant role in public policy development, including alternative energy issues such as those associated with ethanol.

6.1.3 Federal Trade Commission (FTC)

Finally, there is the Federal Trade Commission (FTC). The FTC has various regulations for certain aspects of retail dispenser labeling of transportation fuels. The most common of these is the requirement for octane posting on gasoline dispensers. The FTC has also promulgated regulations which govern certain aspects of the labeling requirements for alternative fuels, including E85.

The ethanol industry is very sensitive to labeling requirements because poorly designed labels may not convey the appropriate information, or worse, could be seen as some type of warning or cautionary advisory.

6.2 State Regulatory Agencies and Departments

Actions taken to regulate transportation fuels at the state level can also impact ethanol use.

6.2.1 State Fuel Quality Programs

Many states have programs that regulate fuel quality. In some states such as Wisconsin and Colorado these may be specific petroleum inspection programs. In most cases, however, these programs are part of the state's Weights & Measures (W & M) program, which is often part of a state's Department of Agriculture. This has largely been an outgrowth of W & M's historic role in testing retail gasoline dispensers for accurate and full measure. Many states' W & M programs now sample and test gasoline to ensure that it complies with state fuel quality standards. Many states have their own laboratories to perform these services while others may send samples to an independent laboratory under contract to the state. Many states that have petroleum quality regulations and inspection programs rely largely on ASTM Standards to serve as their guidelines for enforcement. In fact, a number of states, for instance, automatically adopt the latest version of ASTM D 4814 *Standard Specification for Automotive Spark-Ignition Engine Fuel*. Consequently, actions taken by ASTM are very important to marketers of transportation fuels in these states. Other states may adopt certain elements of ASTM D 4814 while not enforcing the entire specification. At a minimum, most states that have petroleum inspection programs verify that octane ratings meet what is posted on the pump, test for maximum alcohol content, and usually test for vapor pressure. Some states have the capability to verify all the gasoline requirements set forth in ASTM D 4814.

In general, monitoring and enforcement of fuel quality is positive for responsible marketers, including those who choose to offer gasoline ethanol blends. However there are, or have been, state actions relating to fuel quality enforcement that have been detrimental to market expansion of gasoline ethanol blends. To cite a few examples, at least one state has, in the past, had a requirement that a retail facility newly converting to gasoline ethanol blends shut down their pumps for 24 hours. Obviously this penalized a marketer a day's sales and such precautions have not been found to be necessary. Another example is that some states enforce the same vapor pressure and TV/L20 standards for gasoline ethanol blends that are required of an all hydrocarbon gasoline. Since ethanol addition affects the vapor pressure and TV/L20 of the gasoline to which it is added, such requirements may make it necessary to have a specially formulated base gasoline to which the ethanol is added. In addition, many marketers of gasoline ethanol blends do not have the capability to test for such requirements. This discourages them from blending ethanol, fearing that they cannot verify a fuel's compliance, even though it may meet the necessary standards.

6.2.2 State Environmental Agencies/Departments

Each state typically has some type of environmental control agency or department. The names vary from state to state with such designations as "Department of Environmental Quality" (e.g., Montana), Environmental Protection Agency (e.g., California), or Department of Environmental Protection (e.g., Maine). In some cases the agency may be part of another department such as a state's Department of Natural Resources (e.g., Wisconsin) or Department of Health (e.g., Colorado). Regardless of the name or organizational structure, these departments are all charged with protecting the environment in their state. This includes, among other things, air quality and drinking water quality. The authority level, as well as the activity level, of these departments and agencies vary among states. Generally speaking, states with the greatest environmental challenges tend to have environmental agencies that are the most active, and with the most authority.

States may take various actions to regulate transportation fuels. State law and regulations of

transportation fuels for environmental purposes are preempted by U.S. EPA regulations. Therefore states cannot adopt environmental fuel standards that are more stringent than federal requirements without EPA approval. The current exception is the State of California. Under the original Clean Air Act, California, due to its significant air quality problems, was given authority to establish its own stricter environmental controls on transportation fuels. As a result, California has led the nation in adopting stricter clean gasoline standards.

Generally, EPA approval of state programs requiring fuel standards that are more stringent than U.S. EPA's is sought through the State Implementation Plan (SIP) process. States which have areas that are not in attainment for regulated pollutants must file a SIP with EPA to demonstrate how they will bring those areas into compliance. A SIP usually includes actions on both stationary (e.g., power plants, refineries, manufacturing plants) and mobile sources (i.e., automobiles, trucks).

In the case of mobile sources, a SIP will, among other requirements, often include fuel requirements aimed at reducing evaporative and/or exhaust emissions. The types of actions a state could take, in their SIP, that might impact ethanol, could include such items as opting into, or out of, the federal RFG program, developing some version of their own RFG program (e.g., California) or requiring reductions in the vapor pressure of gasoline, especially in summer months (e.g., Detroit area in Michigan and Kansas City, Missouri).

The aforementioned items can affect ethanol use in either a positive or negative way. For instance, if a state opts into the federal RFG program this could result in increased use of ethanol. Conversely, if they adopt a low vapor pressure gasoline regulation this could restrain the use of ethanol since ethanol increases vapor pressure. In addition, these fuels, often called "boutique fuels", tend to fragment the fungibility of the petroleum distribution system because such fuels are not interchangeable with other fuels. This, in turn, requires utilization of more terminal tanks which might otherwise be used for ethanol storage.

The boutique fuels issue has been studied as requested in the National Energy Policy ⁽¹⁾ document. Various options have been considered including offering a menu approach from which states could select a specified option.

There are also actions that a state could take, unrelated to a SIP, that could affect ethanol demand. The most obvious of these is the state bans on the use of MTBE. California, New York, and at least a dozen other states, have implemented bans on MTBE. Some of these bans have already taken effect, while others will be implemented in the 2003 to 2005 time frame. Many refiners who use MTBE for its octane value, or for compliance with fuel regulations, may turn to ethanol as a replacement for MTBE.

6.3 Counties and Municipalities

Most counties and municipalities do not, as a general rule, adopt environmental fuel standards. They tend to rely on the state government to address these often complex issues. However, to the extent that a city or county is part of a non-attainment area, their governments will often participate with their state government in developing a SIP.

Also, a number of cities have elected to participate in the "Clean Cities" program. Clean Cities is a locally-based government/industry partnership, coordinated by DOE to expand the use of alternatives to gasoline and diesel fuels.⁽²⁾ Since the Clean Cities program promotes alternatives to gasoline, such areas often consider purchasing flexible fuel vehicles that can operate on E-85. In some cases municipalities may install E-85 fueling equipment for such fleets or work with a local gasoline retailer or fleet facility to install tanks and dispensers for E-85.

6.4 National Conference on Weights & Measures

The National Conference on Weights and Measures, Inc. (NCWM) is a national professional organization dedicated to developing consensus on standards to fairly meet the needs of consumers, businesses, regulators and manufacturers nationwide. In partnership with the Office of Weights and Measures of the National Institute of Standards and Technology (NIST), NCWM strongly focuses on creating usable, real-world applications of those standards.⁽³⁾ NIST provides technical support to the committees; publishes NCWM Handbook 44, *"Specifications, Tolerances and Other Technical Requirements for Weighing and Measuring Devices,"* and NCWM Handbook 130, *"Uniform Laws and Regulations"*.

NCWM drafts guidelines and model regulations that are often adopted, in whole or in part, into state laws and regulations. Consequently, their actions on transportation fuels can affect ethanol usage.

In particular, NIST Handbook 130 contains a “*Uniform Engine Fuels, Petroleum Products, and Automotive Lubricant Regulation*”. Included within this regulation are definitions for denatured fuel ethanol, E-85 fuel ethanol, ethanol, gasoline-alcohol blends, gasoline-oxygenate blends, oxygen content of gasoline, and oxygenates. The regulation itself specifies standards that gasoline containing oxygenates must meet, as well as guidelines for E-85.

In addition, the regulation provides specific requirements for pump labeling of MTBE, ethanol, and other oxygenates. Since states may adopt these regulations, how ethanol is treated in them can be very important.

The NCWM process provides for input from industry and, in fact, many petroleum and ethanol industry representatives are associate members of NCWM.

The process for adopting or changing a regulation usually starts at the region level[†] and a region will request the NCWM Laws & Regulations (L&R) Committee to put the request on their agenda. The item will then be taken up at the annual NCWM Interim meeting and finally, at the annual NCWM National Conference. Some issues see action very quickly. However, contentious issues can sometimes take a few years to be resolved.

[†]There are four regional Weights & Measures associations, Northeast Weights & Measures Association, Central Weights & Measures Association, Southern Weights & Measures Association, Western Weights & Measures Association

Section 6 References

1. National Energy Policy Group. 2001 *National Energy Policy*. May.
2. U.S. Department of Energy, Office of Transportation Technologies. 1996. *The Road to Clean Cities*. February.
3. National Conference on Weights and Measures. 2002. *NCWM: A Far-Reaching Mission*. www.ncwm.net/mission/html. November.
4. Environmental Protection Agency. 2002. *Mobil Source Air Toxics*, <http://www.epa.gov/otaq/toxics.html>

Section 7

E-85 Issues

7.0 E-85 Issues

The term E-85 is the currently used term to denote fuels containing 75 v% to 85 v% denatured ethanol. The remainder of the blend is typically comprised of either CG or RFG.

The auto manufacturers have been producing an increasing number of Flexible Fueled Vehicles (FFVs) capable of operating on E-85, 100% gasoline, or any mixture of the two. There are now over two million such vehicles on the road. However there currently are fewer than 200 E-85 fueling facilities. ⁽¹⁾

The guiding industry specification for this fuel is ASTM D 5798 *Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines*.

The former American Automobile Manufacturers Association also developed their own specification for E-85 ⁽²⁾ most of which is incorporated into ASTM D 5798. The following table lists the most important property requirements from ASTM D 5798.

The importance of the specified properties is as follows:

Table 7-1 Requirements for Fuel Ethanol (Ed75-Ed85)

Properties	Class 1	Class 2	Class 3
Ethanol + higher alcohols, min,volume %	79	74	70
Hydrocarbon/aliphatic ether,volume %	17–21	17–26	17–30
Vapor pressure, kPa	38–59	48–65	66–83
Vapor pressure (psi)	5.5–8.5	7.0–9.5	9.5–12.0
Lead, max, mg/L	2.6	2.6	3.9
Phosphorus, max, mg/L	0.2	0.3	0.4
Sulfur, max, mg/kg	210	260	300
All Classes			
Methanol, volume %, max		0.5	
Higher alcohols (C3–C8), max,volume %		2	
Acidity, (as acetic acid CH ₃ COOH), mass % (mg/L), max		0.005 (40)	
Solvent-washed gum content, max, mg/100 mL		5	
pHe		6.5 to 9.0	
Unwashed gum content, max, mg/100 mL		20	
Total chlorine as chlorides, max, mg/kg		2	
Inorganic chloride, max, mg/kg		1	
Copper, max, mg/L		0.07	
Water, max, mass %		1.0	
Appearance		This product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at ambient temperature or 21°C (70°F), whichever is higher.	
<i>Source:ASTM D 5798</i>			

Volatility: The ASTM volatility class, ethanol content, and hydrocarbon content is altered seasonally

to adjust the vapor pressure of the fuel. For instance, in the warmer months, E-85 would contain more ethanol and have a vapor pressure of 5.5 to 8.5 psi. However, in the colder months, the blend would contain less ethanol (actually E-75) and more gasoline, to improve cold start and warm up performance. Similar to gasoline specifications, a volatility class is assigned for each month in each state, or in some cases, portions of a state.

Lead: Lead compounds are no longer used in transportation fuels and must be limited to protect the catalyst in the vehicle's catalytic converter.

Phosphorus: Phosphorous also deactivates exhaust catalysts and must therefore be limited to trace amounts.

Sulfur: Sulfur content is limited to protect against engine wear and deterioration of engine oil as well as to protect exhaust system parts and catalytic converters.

Methanol Volume % Maximum: The maximum methanol content of ethanol is limited because methanol, in higher quantities, is an unacceptable contaminant. Methanol is less tolerant to water and may be aggressive to certain metals and elastomers found in automobile fuel systems and retail fuel dispensing equipment.

Acidity: Low molecular weight organic acids such as acetic acid (CH_3COOH) are corrosive to certain metals and must be kept to low levels.

Solvent-Washed Gum: Solvent-washed gum can contribute to fuel system deposits. The impact of solvent washed gums for ethanol, in modern engines, is not well defined. However, the test used detects high boiling, heptane insoluble impurities and helps lower solvent gum levels in the final fuel blend.

pHe: The pHe test procedure was originally developed by General Motors Corporation. A modification of the test procedure and a pHe standard was later adopted by ASTM. Very low levels of highly acidic compounds in ethanol may not always be detected by other test procedures. The pHe test, and standard, were adopted to address this issue. Fuel grade ethanol with a pHe below 6.5 may contribute to failure in fuel pumps and fuel injectors due to corrosive wear. If the pHe is above 9.0, it may have a deleterious effect on plastic parts in the fuel system. These effects are more pronounced on high level blends such as E-85.

Unwashed Gum: The unwashed gum content limit is intended to limit high boiling contaminants, yet allow the use of deposit control additives utilizing carrier oils. Also, the difference between unwashed gum content and solvent washed gum content can be used to assess the presence and amount of non-volatile material in the fuel.

Chlorine and Inorganic Chloride: Both inorganic chloride and organic chlorine are corrosive to many metals and their presence must be minimized.

Copper Content: Copper is a catalyst for oxidation of hydrocarbons at low temperatures. It contributes to a faster rate of gum formation. Its presence in fuel ethanol, and gasoline, must therefore be kept to very low levels.

Water Content: Blends of fuel ethanol and gasoline have a limited solvency for water. This solvency can be affected by the ethanol content, temperature, and aromatic content of the gasoline in the blend. Since E-85 is predominately ethanol, it can suspend much more water than an E-10 blend. High water levels could have a deleterious effect on some fuel system parts.

Appearance: Strong discoloration, phase separation, or precipitates are indicative of contamination.

The following table provides a comparison of the typical properties of E-85 compared to conventional gasoline.

Table 7-2 Comparison of E-85 Properties to Gasoline Properties		
Property	Gasoline (87 Octane)	E-85
Chemical composition	C ₄ to C ₁₂ chains	*
Main constituents (% by weight)	85-88C, 12-15H	57C, 13H, 30 O ₂
Octane (R+M)/2	86-92	96
Btu/Gallon	114,200	~81,700
Gasoline gallon equivalent	1	1.4
Relative tank size to yield driving range equivalent to gasoline	1	tank is 1.4 times larger
Reid vapor pressure (psi)	8-15	6-12
Specific gravity (60/60°F)	0.72-0.78	0.78
Vehicle power	standard	3-5% power increase
Stoichiometric air/fuel ratio (by weight)	14.7	10.0
* depends on percentage and type of the hydrocarbon fraction		
<i>Source: The Current Fuel Ethanol Industry - Transportation, Marketing, Distribution, and Technical Considerations, DAI, May 2000</i>		

Perhaps the most important differences between E-85 and gasoline are that E-85 has a much higher octane value and a lower energy content.

Current flexible fueled vehicles are not optimized to E-85 operation but rather to accommodate the use of gasoline or E-85. This results in lower compression ratios to allow for the use of 87 octane gasoline. An engine optimized for E -85 would have a much higher compression ratio to take advantage of E-85's 96 octane (R+M)/2.

E-85 contains less energy and consequently uses up to 1.4 gallons of E-85 to travel the same distance that could be achieved on 1 gallon of gasoline.

Finally and perhaps most importantly, E-85 requires additional infrastructure. In some cases, properly prepared existing tanks may be used for storage. In many cases, however, additional tanks must be installed. This has been one of the primary impediments to expanding the E-85 fueling infrastructure. There are also special recommendations for certain other equipment which are specified in “*Handbook for Handling, Storage, and Dispensing E85*” which was prepared by the National Renewable Energy Laboratory (NREL) and the National Ethanol Vehicle Coalition (NEVC). This document is available via the Internet at www.e85fuel.com.

The NEVC has been the driving force in attempting to expand the E-85 fueling infrastructure.

Section 7 References

1. Alternative Fuels Data Center. U.S. Department of Energy. 2002. <http://www.afdc.doe.gov>.
2. American Automobile Manufacturers Association. 1997. *Specification for Fuel Ethanol (E_d75-E_d85) As Dispensed to Vehicles*.

Section 8
E diesel™ Issues

8.0 E diesel™ Issues

Over the past few years there has been growing interest in developing a diesel ethanol blend, or so called E diesel™. E diesel™ is a blend of standard No. 2 diesel meeting ASTM D 975 “*Standard Specification for Diesel Fuel Oils*” and up to 15 v% denatured ethanol meeting ASTM D 4806 “*Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*”. In addition, E diesel™ contains a proprietary additive package to keep the ethanol from separating from the blend as well as maintaining other important fuel properties such as cetane quality and lubricity.

The driving forces behind the interest in commercializing E diesel™ relate to energy policy, the environment, and agriculture. Tests have shown that the use of E diesel™ can reduce exhaust emissions of some regulated pollutants, especially particulate matter (PM). Test results comparing E diesel™ to No. 2 diesel have shown the following:

- Tests at the Colorado School of Mines showed NO_x was reduced by 4-6%, PM by 33-40%, and CO by 23% (1)
- Tests by Oak Ridge National Laboratory (SAE Paper # 2001-01-2018) showed a significant drop in PM but an increase in CO and total hydrocarbons (THC), with a negligible effect on NO_x emissions. (2)
- Testing at Argonne National Laboratory (SAE Paper # 2001-01-1937) found that adding ethanol to diesel decreases PM emissions. NO_x emissions are decreased under certain torque and operating conditions and generally THC emissions increased (3)

In addition, since the ethanol in E diesel™ is renewable it would help reduce greenhouse gas emissions. Also, using ethanol in diesel will reduce imports of oil and/or finished diesel fuel, thereby reducing energy dependency and improving the national trade balance. Finally, since ethanol is currently produced primarily from corn, there would be an economic benefit to agriculture and rural America.

But E diesel™ is currently in the research phase. There are a number of open technical issues to be addressed. Currently there is no consensus developed specification standard for E diesel™. The following table compares the typical properties of E diesel™ to standard No. 2 diesel.

Table 8-1 Comparison of Typical Properties -No. 2 Diesel to E diesel™

Property	Test Method	No. 2 diesel	E-diesel
Flash Point min. (C/F).....	ASTM D93	52°/125.6°	10°/50°
Water & Sediment, % max.	ASTM D1796	0.05	?
Distillation % vol rec. T-90 (C) max	ASTM D 86	332	311
Kinetic Viscosity, 40 C (cSt)	ASTM D445	1.9-4.1	1.9-4.1
Ash (%) max	ASTM D482	0.01	0.01
Sulfur (%) max (on-road).....	ASTM D2622	0.05	0.05
Sulfur (%) max (off-road)	ASTM D2622	0.50	0.50
Copper Corrosion @ 3 hr max	ASTM D130	#3	#3
Cetane Number, min	ASTM D613	40	40
Cetane Index, min	ASTM D4737	45	42
Cloud Point (C/F).....	ASTM D2500	†	4.4°/40°
Ramsbottom Carbon, 10% res.	ASTM D4530	0.35	0.22
API Gravity, max	ASTM D287	39	38
Lubricity (g) min (SBOCLE,g)	ASTM D6078	3100	3100
Accel. Stability, pass/fail test	Octel F-21	Pass	Pass
LTFT at -11 C, pass/fail test	ASTM D4539	Pass	Pass
#2 diesel fuel vol (min/max)		100%	79-89
Ethanol vol (min/max)		0%	7-15
Proprietary additive vol % (min/max)		n/a	0.2-5%
Pour Point min. (C/F).....			-17.7°/0°

NOTES

- Due to the low flash point of E-diesel it should be treated as a Flammability Class 1 liquid (i.e. similar to gasoline).
- Since ethanol has a lower btu content than No. 2 diesel, the btu content of E-diesel will be lower than No. 2 diesel. This will vary dependent upon the volume % ethanol present in the blend. The actual effect this may have on fuel economy is dependent upon the engine type and duty cycle.

† Footnote from ASTM D 975: It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. However, satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6°C above the tenth percentile minimum ambient air temperature for the area in which ambient temperatures for U.S. locations are shown in Appendix X2. This guidance is general. Some equipment designs or operation may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.

Source: ASTM D 975 Standard Specification for Diesel Fuel Oils and “Ediesel - The Need for a Specification”, Downstream Alternatives Inc. presented to Central Weights and Measures Association Annual Conference, April 30, 2002

You will note from the previous table that there are a few property changes that result from adding ethanol to diesel. These properties and other fuel property issues are discussed below.

Flash Point: The flash point of a fuel is not related to engine performance but rather legal requirements and safety precautions in handling and storage. It is also often specified in fire regulations and, in some cases, insurance requirements. The flash point of No. 2 diesel is typically 125° F (52°C). The addition of ethanol to diesel, even small amounts, lowers the flash point to ~ 50°F (10°C). The concern here is the flammability of the vapors in the fuel tank head space. In the case of No. 2 diesel, there are very few vapors and so the vapor mixture is too lean to ignite. In the case of gasoline, there are significant levels of vapors in the head space and the vapor mixture is too rich to ignite. Unfortunately, in the case of E diesel™, the low flash point results in a vapor mixture that will ignite. The flammability limits are generally called the upper and lower explosion limits. The lower limit represents the concentration in air below which the mixture will not support combustion. The upper limit represents a concentration where the mixture becomes too rich to support combustion. The flammability limits for a given fuel need to be determined experimentally. They are approximately 0.5 and 2 times the concentration of a stoichiometric mixture in air. A stoichiometric mixture is one for which sufficient air is available to burn all of the fuel with no excess air remaining. The vapor concentration above the liquid depends on the temperature. As the temperature is increased, the vapor pressure of the mixture increases. The lower explosion limit is the temperature where the vapor pressure of the mixture establishes a concentration in air that will just support combustion. The upper explosion limit is likewise set by a higher temperature, above which the concentration of vapor in air is too rich to burn. In a study by Battelle⁽⁴⁾, flammability limits were measured for neat ethanol, neat diesel, and blends of E diesel™ with 10%, 15%, and 20% ethanol and no co-solvent. Battelle concluded that a combustible mixture of fuel vapors is present in fuel tanks at temperatures between about 55° F and 108° F regardless of the percentage of ethanol present. The flash point of E diesel™ is one of the major technical hurdles that will need to be addressed before E diesel™ can be commercialized.

Cloud Point, Pour Point and Cold Flow Properties: Cold flow properties are quantified in the U.S. by cloud point and pour point. Cloud point is the temperature at which initial crystallization or phase

separation (i.e. freezing) of the fuel begins (because diesel fuel is a mixture of many components it does not have a well defined freezing point but solidifies over a wide temperature range). Pour point is the temperature below which the fuel will not pour, using a definition specific to ASTM D 97 *Standard Test Method for Pour Point of Petroleum Products* procedure. Many conventional diesel fuels must be modified by blending with No. 1 diesel or kerosene, or low temperature flow improving additives, during winter, in the northern states to avoid phase separation or fuel gelling.⁽⁵⁾ Because of the very low freezing point of ethanol relative to diesel fuel it might be expected that E diesel™ would have improved low temperature flow properties, as long as the ethanol remains soluble. All emulsifier manufacturers claim that their products make ethanol soluble to very low temperatures. In fact most additive manufacturers claim improved low temperature performance.⁽⁵⁾ Cloud point may not be a good flow property indicator for E diesel™. This is because, though ethanol may change the temperature for cloud point, the ethanol is actually still liquid and will flow through the filters. It is not necessarily, as with diesel, an indication of the formation of wax crystals. It may therefore be desirable to utilize a cold filter plugging point (CFPP) test for E diesel™ property measurements.⁽⁵⁾

Lubricity: ASTM D 975 does not currently include a minimum lubricity requirement. However, lubricity is very important in diesel engine applications because portions of the fuel system (e.g., fuel pumps) depend on the fuel for lubrication. Consequently, several diesel engine manufacturers specify a minimum lubricity level for fuel used in their engines. The addition of ethanol to diesel may decrease the lubricity of the fuel. However, lubricity additives either are, or can be, incorporated into the additive treatment package if necessary. There are four tests⁽⁶⁾ used to measure the lubricity of diesel fuels. They are:

HFFR: *ASTM D6079 High Frequency Reciprocating Rig (HFFR)* - This test involves a ball on plate configuration, with the contacting surfaces submerged in the test fuel. The ball oscillates on the plate, resulting in a measurable wear scar. The design of the test was intended to maximize boundary lubrication conditions and minimize the effect of fuel viscosity. This test can be run at either 25° C or at a standard temperature of 60° C.

BOCLE: ASTM D5001 Ball on Cylinder Lubricity Evaluator (BOCLE) - This test was developed to predict the lubricity performance of aviation fuels. Point contact occurs between a stationary ball on top of a rotating cylinder, which has the lower portion submerged in the test fuel. A fixed load is applied to force the ball into contact with the cylinder. The wear scar of the ball is used to indicate the lubricity of the test fuel. This method is generally characterized by higher levels of corrosive and oxidative wear.

SLBOCLE: ASTM D6078 Scuffing Load Ball on Cylinder Lubricity Evaluator (SLBOCLE) - This method uses the same bench rig as the ASTM D5001 method. However, in this method the load is not fixed. The load is varied to determine the minimum load at which scuffing will occur and a wear scar will start to form on the ball. This is intended to simulate the transition from mild wear to scuffing or adhesive wear. Because the test must be run with several different loadings, this method can be time consuming.

LZ BOCLE: Lubrizol Scuffing Load Ball on Cylinder Lubricity Evaluator (LZBOCLE) - The bench rig used in both the ASTM D5001 and the ASTM D6078 methods is also used in this test method. To promote the occurrence of scuffing or adhesive wear the conditions of the original ASTM D5001 are altered to include a higher load, higher speed and increased humidity. This test was designed to provide an indication of scuffing wear, without the repetitive testing required in the ASTM D6078 method.

Study in this area is ongoing and more demonstrative work will be necessary as demonstration of good lubricity properties would be a prerequisite for obtaining acceptance of E diesel™ under manufacturer warranty coverage.

Fuel Stability: In standard No. 2 diesel, water promotes corrosion and microbiological growth may occur at a fuel-water interface (7). In the case of E diesel™, additive manufacturers have presented

information that indicates their additive packages would increase water tolerance of E diesel™, up to 3% water in some conditions. There are two issues here. First, the engine and equipment manufacturers want to see more detailed study of the various additive's ability to keep E diesel™ properly blended under the wide variety of circumstances that could be encountered in actual field conditions. The second issue is the effect that ethanol, the additive package, and the increased water content may have on oxidation and biological stability. Additional testing will be needed to address these issues.

Vapor Pressure: Vapor pressure maximums are not specified for No. 2 diesel because the vapor pressure of standard diesel fuel is typically less than 0.1 psi. The addition of ethanol to diesel fuel will raise its vapor pressure. Although this is not expected to create operability problems, the OEMs would like to see additional study to confirm this. For example, would increased fuel volatility lead to fuel pump cavitation? A second issue is to what extent E diesel™ would result in higher evaporative emissions. Since diesel trucks and equipment are not equipped with evaporative emissions controls, any increase in evaporative emissions needs to be quantified.

Operability Issues: The Original Equipment Manufacturers (OEMs) would like to be certain that their engines would operate at comparable performance levels on whatever fuel is permitted to be used in them. As an example, at comparable engine speeds and torque curves, one recent study (8) showed that a Cummins C8.3 engine operating on E diesel™ could not match the torque/speed combinations recorded for No. 2 diesel at engine speeds below 1500 rpm, without significantly increasing fuel flow. This same study showed an increase in exhaust valve seat temperatures. If it is necessary to increase E diesel™ fuel flow to match torque/speed combinations this would be an issue because increasing the full-load fueling of emission certified engines is prohibited by law.

Materials Compatibility: There are numerous components in a diesel fueling system including fuel pumps (at least three major configurations), fuel injectors, and fuel lines, fittings, and pressure relief valves. These components encompass various metals and elastomers. While field demonstrations in

the U.S. have not identified major problems, much more testing, both field demonstrations and controlled laboratory tests, need to be undertaken to demonstrate to the OEMs that materials compatibility will not be a problem.

Energy Content: The energy content of E diesel™ is much less than No. 2 diesel. A typical diesel fuel would, based on lower heating values, have 132,000 btu/gal (36.6 MJ/L). Adding 10 v% ethanol would reduce the energy content to 126,442 btu/gal (35.1 MJ/L) , a decrease of 4.2%.⁽⁵⁾ In some applications, this may not translate to an energy loss of that level, while in others it may. The actual increase in fuel consumption resulting from E diesel™'s lower energy content will depend on both engine type and operating conditions.

OEM Warranties and Fuel Recommendations: Currently no engine manufacturers have indicated they will extend warranty coverage to their equipment when operating on E diesel™. They believe there are simply too many unanswered questions as well as the potential for liability exposure due to the increased flammability range of E diesel™. At least one manufacturer ⁽⁹⁾ has specifically advised against using alcohol in diesel. Engine manufacturers will not be prepared to extend warranty coverage, or even adopt a position of neutrality, until the open technical issues surrounding E diesel™ are resolved. One major diesel equipment manufacturer, John Deere and Company,⁽¹⁰⁾ is initiating a major E diesel™ research project that will encompass both controlled tests and field demonstrations. The test will encompass three engine types and three injection technologies. While this research program will likely answer many questions, it is more of a starting point. It will likely eliminate the need to study some areas, but will also likely reiterate the need to intensify focus in others.

Health Effects Testing: E diesel™ cannot currently be offered for on-road use because it has not yet undergone EPA Health Effects Testing Requirements (current on-road use is for demonstration projects permitted by EPA). The 1990 Clean Air Act Amendments† resulted in new regulations requiring health

† 40 CFR Part 79 Registration of Fuels and Fuel Additives

effects testing. Consequently, EPA fuel registration now requires various health effects testing. Tier 1 of this process focuses on regulated and unregulated emissions and a literature search for such information. Tier 2 of the process requires 90 day inhalation studies (laboratory animals) on carcinogenicity, mutagenicity, reproduction toxicity, teratogenicity, and neurotoxicity. Based on the results of Tier 1 and 2 of the process, EPA may, at its discretion, require additional testing under Tier 3. Based on experience with other such efforts ⁽¹¹⁾, Tier 1 of the process could take 6 to 8 months and cost \$250,000. Tier 2 of the process would require a minimum of 12 months and costs could exceed \$1.5 million.

E diesel™ Consortium: A group of E diesel™ stakeholders have formed the “E diesel™ Consortium” to pool resources to address technical issues and health effects testing. The E diesel™ Consortium is attempting to not only address the technical issues and health effects testing of E diesel™, but also to identify a commercialization pathway for this fuel. At the time this document was prepared, the E diesel™ Consortium was preparing to establish a website, but a URL was not yet available. The E diesel™ Consortium website, once established, will be accessible through a link from the Renewable Fuels Association website (www.ethanolrfa.org).

Nation Renewable Energy Laboratory (NREL): NREL has also recently put an E diesel page on their website (www.nrel.gov) Reference #5 for this section, which provides an excellent and more detailed discussion of technical barriers to commercialization of E diesel™, is also available from NREL.

Recommendations: Obviously, unresolved technical issues and EPA health effects testing will be expensive and also require significant personnel resources. The DOE, through its National Renewable Energy Laboratory (NREL), was instrumental in bringing stakeholders together to form the E diesel™ Consortium and also covered the expenses of several initial meetings and conference calls. While the consortium expects to pool resources to begin to address the many aforementioned issues, it is doubtful that required resources could be provided solely by the members of the E diesel™ Consortium. Based on this, the following recommendations are offered:

- *The DOE, either directly and/or through NREL, should continue to participate in the E diesel™ Consortium. This provides the necessary information flow between industry stakeholders and government.*
- *To the extent possible, the National Laboratories should undertake whatever portion of the necessary testing that is within their capabilities.*
- *If the DOE wishes to see E diesel™ commercialized, more dialogue between the Department and the engine manufacturers would be beneficial.*
- *To the extent possible, and where industry is prepared to match funding, DOE should continue to look for areas to fund worthwhile research projects to address the many unresolved technical issues associated with E diesel™.*

Section 8 References

1. AAE Technologies and Octel Starreon. 2001. *O2 Diesel*. September.
2. Kass, S.M. *et.al.* 2001. *Emissions from a 5.9 Liter Diesel Engine Fueled with Ethanol Diesel Blends*. SAE Paper #2001-01-2018. May 7.
3. Coile, R. *et.al.* 2001. *Effects of Ethanol Addition on Diesel Particulate and NOx Emissions*. SAE Paper #2001-01-1937. May 7.
4. Graboski, Michael. 2001, *Summary and Analysis of Study “Flammability Limits for Ethanol/Diesel Blends.”* Memo to Bob Dinneen, Renewable Fuels Association. June 22.
5. McCormick, Robert L. and Richard Parish. 2001. *Advanced Petroleum Based Fuel Program and Renewable Diesel Program*. National Renewable Energy Laboratory. Prepared for the U.S. Department of Energy, Office of Heavy Vehicle Technologies, Office of Fuels Development. November.
6. Corwell, Keith and Mitchell Jackson. 2002. *Lubricity and Injector Pump Wear Issues with E diesel Fuel Blends*. SAE Paper #2002-01-2849. October 21.
7. ASTM D 975 *Standard Specification for Diesel Fuel Oils*.
8. Mendoza, Michael and Peter Woon. 2002. *E-diesel Effects on Engine Component Temperature and Heat Balance in a Cummins C8.3 Engine*. SAE Paper #2002-01-2847. October 21.
9. Cummins Inc. Website. www.cummins.com/na/pages/en/customerassistance/faq/answers.cfm?uuid=00099E71-550E-1B8E-BCF080C4A8F00000
10. John Deere research proposal presented to the Renewable Fuels Association, no date.

Section 9
Fuel Cell Issues

9.0 Fuel Cell Issues

Fuel cells are electrochemical devices that combine hydrogen and oxygen to generate electricity. They do so with much less noise and pollution than internal combustion (IC) engines. Additionally, fuel cells are more energy efficient than IC engines. The unique combination of efficiency and ultra-low emissions is why every major automaker has a fuel cell development program.

There are different types of fuel cells, such as Solid Oxide Fuel Cells (SOFC), Molten Carbonate Fuel Cells (MCFC), and Proton Exchange Membrane Fuel Cells (PEMFC). Due to lower operating temperature requirements, the fuel cell of most interest for transportation application is the PEMFC.

All fuel cells are essentially fueled with hydrogen. It is the source of the hydrogen, and how it will be delivered to the fuel cell, that is currently unresolved.

In transportation applications, hydrogen could be stored on-board the vehicle. This would require the hydrogen to be produced, stored and then delivered to the vehicle. The vehicle would need to have hydrogen storage tanks, which typically store hydrogen in the 5,000 to 10,000 psi range, in order to store enough hydrogen to have a reasonable range between refuelings.

A second option is to store a liquid fuel (hydrogen carrier) “on board” and utilize a reformer to extract the hydrogen from the fuel for delivery to the fuel cell. Liquid fuels that could fill this role include gasoline (or at least specific gasoline hydrocarbons), methanol, natural gas, and ethanol. Some recent work has even focused on diesel fuel. Other hydrogen carriers that have at least been studied include ammonia (NH_3)⁽¹⁾ and sodium borohydride (NaBH_4)⁽²⁾. Reforming technology could also be used in stationary applications. Hydrogen could also be supplied from water using electrolysis. This is currently not energy efficient but perhaps could be if the electricity for the hydrolysis were provided from photovoltaics or wind generated electricity.

It is unclear, at this point, what the predominant source of hydrogen will be and, in the case of transportation applications, whether the hydrogen will be stored on-board or reformed on-board.

Ethanol offers some very positive attributes as a fuel (hydrogen carrier) for fuel cell applications including the following:⁽³⁾

- Ethanol blends seamlessly with gasoline fuels to create an improved fuel cell fuel that is easily stored and dispensed. These blends can be varied over time, providing fuel source flexibility.
- Ethanol, a renewable fuel, used in fuel cell vehicles or for stationary power plants, generates far fewer greenhouse gases than conventional fuels such as gasoline or natural gas.
- Ethanol’s distribution infrastructure is complete to the terminal level, meaning that only very limited investment in local distribution could enable ethanol to power fuel cells for remote residences and cell towers far from the electric grid.
- Unlike other fuel cell alternative fuels like hydrogen or methanol, ethanol has a very positive environmental, health, and safety footprint with no major uncertainties or hazards.
- The technology to use ethanol in fuel cells already exists and has been demonstrated. Only minor changes are required to existing systems to introduce ethanol as a fuel cell fuel.

Similarly, a consultant study commissioned by the California Fuel Cell Partnership ⁽⁴⁾ found that:

- A “major advantage” of ethanol is its compatibility with gasoline reformer technology and its flexibility to be used neat (i.e., only ethanol) or in a range of gasoline/ethanol blends.
- Flexibility, combined with ethanol’s compatibility with the gasoline infrastructure, means that ethanol can be optimized regionally and according to ethanol economics and availability vs. gasoline. This is the only proposed fuel cell vehicle fueling strategy that does not require the commitment of major infrastructure investments for a single fuel.

- An ethanol reformer could be simpler, more reliable, and less costly than a gasoline/multifuel reformer, increasing ethanol's attractiveness as a neat fuel for fuel cell vehicles.

Ethanol's one major drawback, at this point, is that it is not perceived as being widely available compared to other options. However, it could be used at varying levels in a gasoline blend for fueling a fuel cell until larger supplies are available.

The ability to reform hydrogen from ethanol has been demonstrated in research projects using multifuel reformers ⁽⁵⁾. This reforming technology is designed to accommodate gasoline, ethanol, and methanol. The current multifuel reformers are not optimized to ethanol use but rather to accommodate the higher hydrocarbon content of gasoline. No reformer has been developed specifically for ethanol use.

The first field demonstration of ethanol in an actual fuel cell application will get underway in early 2003 ⁽⁶⁾. This project is a joint effort between Nuvera Fuel Cells, Caterpillar, and Williams BioEnergy with funds also provided by DOE and the Illinois Department of Commerce and Community Affairs.

This project will use a PEMFC system, but in a stationary application. Nuvera will provide the fuel cell, reformer, and system controls, as well as testing and data acquisition. Caterpillar will provide program management and system controls as well as testing and data acquisition of supporting electronics. Williams BioEnergy will provide the ethanol fuel source and system test facility. The fuel cell will be installed at Williams' ethanol production facility to power their visitors center. The goals of the program are:

- Demonstrate performance and durability.
- Remove technical uncertainties.
- Understand correlation and reduce gaps between stationary and transportation applications.
- Data collection to evaluate economic feasibility.
- Assess commercial viability of total system.

Of course, the fuel cell industry, though no longer in its infancy, is at the beginning of its commercialization effort. There are literally several hundred technical papers presented each year on a variety of fuel cell related topics. With regards to fuel, the path is not yet known.

Ethanol may be able to participate via reforming in a multifuel reformer (both transportation and stationary applications).

The ideal situation would, of course, be a reformer optimized to ethanol use. For one thing, hydrogen from ethanol requires water which means 160-180 proof ethanol could be used. This would result in lower ethanol production costs due to savings from not removing water to reach the 200 proof level. Moreover, compared to gasoline, ethanol is easier to reform, ⁽⁵⁾ it is sulfur free, and can be reformed at lower temperatures.

Argonne National Laboratory's Electrochemical Technology Program has indicated they have the technology, background, and facilities to design an ethanol fuel reformer.⁽⁵⁾ Of course, there are also a number of open technical issues associated with this newly developing potential use of ethanol in fuel cells.

- The optimum water content of the ethanol has not been determined.
- In an ethanol reformer, a denaturant other than gasoline (e.g., methanol) would be preferred to avoid catalyst contamination.
- It is unknown what level of common ethanol contaminants, such as fusel oils, could be tolerated by the catalyst.

With the relative newness of both the fuel cell industry in general, and considering ethanol as a fuel source in particular, it is difficult to offer a definitive issue profile. Much more research and development work is needed.

The Renewable Fuels Association, through its Fuel Cell Task Force has become actively engaged in the fuel cell industry. They have recently developed a white paper ⁽³⁾ which is available on

their website at www.ethanolrfa.org. The DOE has been supportive of developing reformer technology (on a fuel neutral basis). United States Secretary of Energy Spencer Abraham and senior executives of DaimlerChrysler, Ford, and General Motors announced the Freedom Car Partnership on January 9, 2002. ⁽⁷⁾ putting emphasis on fuel cells for transportation application and development of a hydrogen fueling infrastructure. Finally, the DOE has recently released the *National Hydrogen Energy Roadmap* ⁽⁸⁾ which encompasses all aspects of developing a hydrogen infrastructure including production, delivery, storage, conversion, applications, and public education and outreach.

While the widespread commercialization of fuel cells may be a decade or more away, it is clear that if ethanol is to play a role it must be in the game now.

Recommendation: *The development of cellulosic derived ethanol will overcome one hurdle for ethanol, supply availability. If transportation fuel cells gradually replace IC engines, likely in the same time frame cellulosic ethanol production will increase, it will be important that ethanol plays a role as a hydrogen carrier for fuel cells.*

Research with multifuel reformers and an ethanol specific reformer needs to continue. Where possible, DOE should pursue opportunities with industry to further such technologies. Additionally, the EERE should closely coordinate efforts between its Biomass, Freedom Cars and Vehicle Technologies, and Hydrogen, Fuel Cells and Infrastructure Technologies programs to ensure that cellulosic ethanol will have a role in the fuel cell fuels market.

Section 9 References

1. Gay-Desharnais, Sebastien, Jean-Yves Routex, Mark Holtzapple and Mehrad Ehsani. 2002. *Investigation of Hydrogen Carriers for Fuel-Cell Based Transportation*, SAE Paper # 2002-01-0097. March 4.
2. Mohring, Richard, Ian Eason, and Keith Fennimore. 2002. *Performance Bench Testing of Automotive-Scale Hydrogen on Demand™ Hydrogen Generation Technology*. SAE Paper # 2002-01-0098. March 4.
3. Renewable Fuels Association. 2002. *Ethanol & Fuel Cells: Converging Paths of Opportunity*. Prepared by Jeffrey Bentley and Robert Derby. August.
4. California Fuel Cell Partnership. 2001. *Bringing Fuel Cell Vehicles to Market: Scenarios and Challenges with Fuel Alternatives*. Prepared by Bevilacqua Knight Inc. October.
5. Argonne Electrochemical Technology Program. 2002. *Ethanol Fueled Fuel Cell Power*. 2002. Presented at Illinois Department of Commerce and Community Affairs, January 31.
6. Nuvera, Caterpillar, Williams Energy. 2002. *PEM Ethanol Fuel Cell-Utility Interactive System*. May.
7. United States Department of Energy. 2002. *FreedomCar Partnership Plan*. September.
8. United States Department of Energy. 2002. *National Hydrogen Energy Roadmap*. November.

Section 10

Glossary of Acronyms and Commonly Used Terms

10.0 Glossary of Acronyms and Commonly Used Terms

Acronyms

AKI:	Anti Knock Index
API:	American Petroleum Institute
ASTM:	ASTM International (formerly American Society for Testing and Materials)
BATF:	Bureau of Alcohol, Tobacco and Firearms
BOV:	Blending Octane Value
btu:	British Thermal Units
btu/gal:	British Thermal Units per gallon
CO:	Carbon Monoxide
CRC:	Coordinating Research Council
DI:	Driveability Index
DOE:	U.S. Department of Energy
E-85:	Commonly used term to describe ethanol gasoline blends containing 75 v%-85 v% denatured ethanol. This fuel is used in vehicles specifically designed to allow their use.
EERE:	DOE Office of Energy Efficiency and Renewable Energy
EP:	End Point, the distillation temperature at which 100% of a gasoline sample is vaporized.
EPA:	U.S. Environmental Protection Agency
FTC:	U.S. Federal Trade Commission
HC:	Hydrocarbon
LEV:	Low Emissions Vehicle
MCFC:	Molten Carbonate Fuel Cell
mg/L:	Milligram per liter

MMT:	Methylcyclopentadienyl Manganese Tricarbonyl
MON:	Motor Octane Number
MTBE:	Methyl Tertiary Butyl Ether
NACE:	National Association of Corrosion Engineers
NCWM:	National Conference on Weights and Measures
NEVC:	National Ethanol Vehicle Coalition
NO _x :	Oxides of Nitrogen
NREL:	National Renewable Energy Laboratory
OEM:	Original Equipment Manufacturer
ORNL:	Oak Ridge National Laboratory
PEMFC:	Proton Exchange Membrane Fuel Cell
pHe:	Acid strength of acids in ethanol as determined by ASTM D 6423 <i>Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)</i> .
RFA:	Renewable Fuels Association
RFG:	Reformulated Gasoline
RON:	Research Octane Number
RVP:	Reid Vapor Pressure
SAE:	Society of Automotive Engineers
SHED:	Sealed Housing for Emissions Determination
SIP:	State Implementation Plan
SOFC:	Solid Oxide Fuel Cell
T10:	The distillation temperature at which 10% of a gasoline sample is vaporized.
T50:	The distillation temperature at which 50% of a gasoline sample is vaporized.
T90:	The distillation temperature at which 90% of a gasoline sample is vaporized.
TV/L20:	Temperature for a vapor to liquid ratio of 20 as determined by ASTM D 2533 or ASTM D 5188. A measure of a fuel's front end volatility. Also used to assign vapor lock protection classes for gasoline in the ASTM specifications.

ULEV	Ultra Low Emission Vehicle
v%:	Volume Percent
VP:	Vapor Pressure
WWFC:	World-Wide Fuel Charter

Terms

Antiknock Index:	The Antiknock Index (AKI) of a motor fuel is the average of the Research Octane Number (RON) and the Motor Octane Number (MON) or $(R+M)/2$. This is the number displayed on the black and yellow octane decal posted on the gasoline pump.
Blending Octane Value:	The value assigned to a fuel component that will enable its octane contribution to the finished gasoline blend to be predicted. This also enables the octane of the finished gasoline blend to be predicted.
Cetane Index:	The cetane index is an approximation of cetane number based on the properties of the fuel as determined by ASTM D 976 <i>Test Method for Calculated Cetane Index of Distillate Fuels</i> .
Cetane Number:	A measure of the ignition quality of diesel fuel as determined by ASTM D 613 <i>Test Method for Cetane Number of Diesel Fuel Oil</i> .
E diesel™:	A blend of No. 2 diesel meeting ASTM D 975 containing up to 15 v% ethanol meeting ASTM D 4806 as well as 0.2% to 5.0% proprietary additive to maintain fuel properties such as cetane number, lubricity and blend stability.
Flash Point:	The lowest temperature at which vapors from a petroleum product will ignite as determined by ASTM D 56 <i>Test Method for Flash Point by Tag Closed Tester</i> or ASTM D 93 <i>Test Method for Flash Point by Pensky-Martens Closed Cup Tester</i> .
Latent Heat of Vaporization:	The heat required to initiate a change from a liquid state to gaseous state at a constant temperature.

- Motor Octane Number: The octane of a fuel as determined on a laboratory engine test by ASTM D 2700 *Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method*. The MON is associated with high speed and part-throttle knock. If the Motor Octane Number is too low, the driver could experience engine knock during periods of power acceleration such as passing vehicles or climbing hills.
- Octane: A general term for the octane number posted on the retail dispenser. The same as Antiknock Index (AKI).
- Octane Sensitivity: The difference between the research and motor octane numbers (R-M=Sensitivity). Lower sensitivity numbers are desirable, e.g., 10 for 87 AKI unleaded regular.
- Research Octane Number: The octane of a fuel as determined on a laboratory engine test by ASTM D 2699 *Test Method for Knock Characteristics of Motor Fuels by the Research Method*. In general, Research Octane Number (RON) is associated with low to medium speed knock and engine run-on or dieseling. If the Research Octane Number is too low, the driver could experience low speed knock and engine run-on after the engine is shut off.
- Substantially Similar: Section 211 (f) (1) [U.S.C. 7545 (f)(1)] of the Clean Air Act prohibits introducing into commerce or increasing the concentration in use of, any fuel or fuel additive, which is not substantially similar to any fuel or fuel additive utilized for emissions certification of any 1975, or subsequent model year vehicle or engine, unless a waiver is obtained from the EPA. Gasoline-oxygenate blends are considered “substantially similar” up to an oxygen level of 2.7 wt% providing certain other criteria are met.